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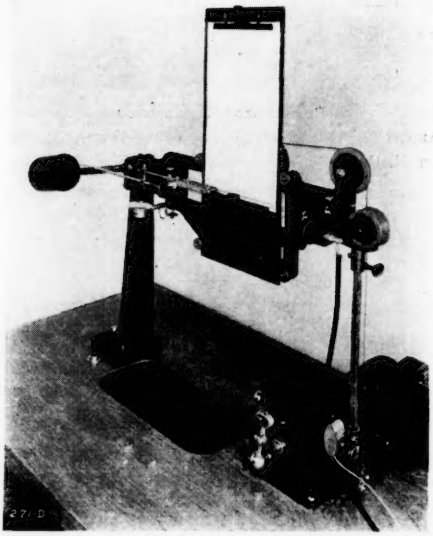

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Publication of

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The Textile Foundation, Inc.

H. M. Chase Added to Warp Sizing Committee

HAROLD M. CHASE, chief chemist and research director, Riverside and Dan River Cotton Mills, Danville, Va., has accepted appointment to the Administrative Committee for the Institute's warp sizing research of which Carl R. Harris, manufacturing engineer, Erwin Cotton Mills Co., Durham, N. C., is chairman. Mr. Chase took an active part in the preliminary organization of this research on the warp sizing of spun rayon and blends of cotton-spun rayon. The other members of the Administrative Committee are Dean Thomas Nelson of North Carolina State College Textile School, where the study is to be conducted, and Dr. William E. Yelland, director of the Institute's previous warp sizing study, now with the research laboratory of Corn Products Refining Co.

At this writing the Administrative Committee has been unable to complete plans for the holding of an open conference of subscribers to the project, and of others who may be interested, as noted in these columns last month. It is hoped, however, to hold it at Raleigh, N. C., Saturday, April 20th. Whatever may be the date decided upon, subscribers, and all others who have indicated the wish to attend, will be notified at least ten days in advance. The research program to be presented will be subject to discussion and revision. Laboratory equipment and methods will also be described, and there will be an opportunity to visit the laboratory and the new building of the Raleigh, N. C., Textile School.

* * *

General Textile Course for College Graduates

THE directors of the Textile Foundation have authorized a special survey of the possibilities of providing a year of training for the textile industry for graduates of engineering schools and colleges who have not been previously associated with this industry. It is proposed that the report will summarize the facts with regard to the needs of such a textile industry preparatory training. The original report on the "Training of Men for the Textile Industry" indicated the possibility of developing a textile industrial preparatory course, which might be given in one or more textile schools to those men who have graduated at colleges or universities where textile instruction was not available.

The proposal does not contemplate a post-graduate year in the ordinary sense, but rather an organized vocational guidance course for young men desiring to enter the textile industry, but who are not acquainted with its general organization, its production and sales practices. The inquiry is in charge of Thomas R. Taylor, a graduate engineer and economist, of Washington, D. C., and will be conducted in co-operation with leaders of the textile industry and of textile education, as has been the case in other surveys undertaken in the field of education by the Foundation. Frederick M. Feiker, Dean of the School of Engineering of George Washington University, and Educational Consultant for the Textile Foundation, will co-operate with Mr. Taylor in the development of the special report.

* * *

A Rayon Scholarship

THE RHODE ISLAND SCHOOL OF DESIGN, Providence, R. I., announces a new scholarship which will make possible a graduate course covering the rayon field. The student to whom it is awarded will be given an opportunity to supplement his school work by actual training and study in the industry itself, through a co-operative arrangement to be developed. This "Atlantic Rayon Scholarship" of $1,200 will be awarded yearly, and, for the first time at the commencement exercises in May, to a senior textile student who in the opinion of the committee possesses those qualities which indicate a future ability as a textile executive. The awarding committee will consist of a representative of the Atlantic Rayon Corporation and members of the faculty of the School.

* * *

Personals

Dr. Edward W. France will end in June his connection of 56 years with the Philadelphia Textile School, during the greater part of which period he was its director. His resignation was presented to and regretfully accepted by the Trustees of the School just prior to the Alumni Association banquet, March 1, at which it was announced, and at which a large gathering of the alumni gave an ovation to Dr. France. His successor, as announced at that function, is M. E. Heard, head of the engineering department of Texas Technological College, Lubbock, Tex. He is a graduate of Georgia Tech. Dr. France is the acknowledged dean of domestic textile school heads. He made the Philadelphia Textile School what it is today. To him hundreds of textile executives and technicians owe their success, and much of that success was due to advice freely provided by Dr. France after they left the school. Perhaps the skilled advice that he gave to them, to other manufacturers and to government representatives has been of as great value to the country as his services as school director. Certainly, the services of no other individual as a textile consultant have been sought and given so frequently. And there is no reason why this young man of 80 years should not continue to serve the industry with his ripe store of knowledge and experience.

(Continued on Pages 228 and 252)

Concerning the Existence of Fractions of the Sericin in Raw Silk

By HENRY A. RUTHERFORD and MILTON HARRIS *

A Textile Foundation Publication

Abstract

Raw silk fibres consist of at least two proteins, silk fibroin and silk sericin. The latter forms a coating over the fibroin and constitutes 15 to 30% of the total weight of the raw fibre. In practical silk processing, the sericin is generally allowed to remain on the fibre until the fabric is ready to be dyed. In this way, it acts as a protective coating for the silk in the weaving or knitting operations.

Removal of the sericin is usually accomplished with hot soap solutions. The results of numerous studies of this process led earlier investigators to a variety of concepts concerning the state and properties of the sericin in the raw silk fibre. Some stated that the sericin is a single protein substance, whereas others claimed it to be a mixture of proteins which they designated as sericins A, B, etc. The latter concept formed the basis for further claims concerning the desirability of retaining certain fractions of the sericin to improve some ultimate properties of the silk. As many of these claims were based on insufficient experimental evidence, it seemed desirable to make a more extensive investigation of the question of the possible existence of several fractions of the sericin in raw silk.

The results of the present investigation show that the relative yields of the so-called sericins A and B, obtained after treatment of silk in an autoclave, were dependent on the duration of the treatment. Practically all of the sericin removed in the early stages of autoclaving was in the form generally designated as sericin B. On continuing the treatment, this fraction was rapidly converted into the more soluble form, sericin A. Analyses of the fractions, obtained after autoclaving the silk for different lengths of time, showed that the alleged sericins A and B are not definite chemical entities, but are substances whose chemical compositions vary with the duration of the autoclave treatment. It is concluded from these studies that the sericin in raw silk does not exist as a mix-

* Research Associates at the National Bureau of Standards representing the Textile Foundation, Inc.

ture of fractions, but that the fractions are artifacts which result from the hydrolytic decomposition of the naturally occurring sericin during its removal from the raw fibres.

Introduction

RAW SILK FIBRES consist of at least two proteins, silk fibroin and silk sericin. The latter forms a coating over the fibroin and constitutes 15 to 30% of the total weight of the raw fibre. Removal of sericin from fibroin is based on the solubility of the former in hot aqueous solutions. The solubility increases considerably in the more alkaline or acid solutions.

A variety of concepts relative to the nature of sericin and the fractions obtained from it have appeared in the literature. In 1784, one of the first published records on the removal of sericin from silk by the use of alkaline solutions appeared.[1] A number of similar investigations followed until Cramer,[2] in 1865, expanded the scope of the investigations and obtained several proteins by fractionation of a solution of sericin. He suggested that these fractions were decomposition products of the naturally occurring material. Following his findings, Wetzel,[3] Bondi,[4] Fischer and Skita,[5] and Anderlini,[6] studied the removal of sericin from silk and concluded that sericin in raw silk exists in more than one modification, although good experimental evidence to substantiate such a conclusion was lacking. In the above-mentioned investigations, different procedures for the preparation of the sericin solutions were employed, and little analytical work was done to characterize the protein fractions which were obtained. As a consequence, widely different results were reported by the different investigators. For example, Bondi found two fractions in a solution of sericin obtained by boiling silk in water, while Anderlini was able to separate three fractions after a prolonged extraction of raw silk with water at 50° to 60° C.

More recently Sheldon and Johnson[7] isolated two fractions from sericin solutions which had been obtained by autoclaving raw silk in water at temperatures of about 115° C. They concluded that raw silk sericin contains at least two proteins, one of which is soluble and the other insoluble in cold water. Subsequent investigators using the autoclave to remove the sericin appeared to substantiate these findings, and also attempted to define the properties of the isolated fractions. Mosher[8] stated that both fractions are very much alike chemically, but possess different physical properties, especially with respect to solubility. He further noted that the insoluble fraction was converted into a soluble one by boiling in aqueous solution, the conversion being greatly accelerated by increasing the acidity, alkalinity, or temperature of the solutions. Although he concluded that sericin is composed of three distinct fractions, his results could be interpreted to mean that sericin does not exist as a mixture of proteins in raw silk, and that these fractions are decomposition products formed during the process of removal of the sericin from the fibres.

In contrast to some of the conclusions of Mosher, Kaneko,[9] and Ito and Komori[10] found the different sericin fractions to be different chemically. Their results were based on determinations of the nitrogen distribution and the tyrosine contents of the isolated fractions. However, disagreements are found even between the data of these investigators.

For example, Kaneko found that the soluble fraction is especially rich in arginine nitrogen, whereas Ito and Komori found a greater proportion of this nitrogen in the insoluble portion.

From consideration of the previous investigations, it became evident that no satisfactory conclusion concerning the existence of several fractions of the sericin of raw silk could be reached. In the present investigation an attempt was made to throw further light on the question by making a more extensive study of sericin and of the fractions obtained from it.

Experimental Procedure

1. Materials and methods.—Samples of white Japanese silk which had received no previous treatment other than that used in the reeling process were used in this work. The naturally occurring waxes were removed by cold extractions for 24 hours each with alcohol and ether. Analyses of the dewaxed fibre gave the values shown in Table 1. The data for

TABLE 1

Total and amino-nitrogen, tyrosine, carbohydrate, and amino-sugar contents of the dewaxed silk, fibroin and sericin used in the present investigation. The data for sericin were calculated from the analytical data on dewaxed silk and fibroin and from the determined sericin content.

Material	Total nitrogen	Amino nitrogen [a]	Tyrosine	Carbohydrate (as glucose)	Amino sugars (as glucosamine)	Sericin content
	%	%	%	%	%	%
Dewaxed silk	18.29	0.14	10.9	0.67	0.80	23.7
Fibroin	18.73	.09	12.3	0.56	0.30	—
Sericin	16.92	.30	6.3	1.0	2.4	—

[a] Determined by method of Rutherford, Harris, and Smith.[12]

sericin were calculated from the analytical data for the dewaxed silk and fibroin and from the determined sericin content.

Total nitrogen was determined by the micro-Kjeldahl method, and tyrosine by Lugg's method, [11] after an alkaline hydrolysis. The amino-nitrogen content of the fibrous and of the insoluble proteins was determined by the method of Rutherford, Harris, and Smith.[12] The method of Van Slyke [13] was used for the determination of the amino-nitrogen content of sericin solutions. Carbohydrate and amino sugars were estimated by the methods outlined by Sørensen.[14, 15]

2. Preparation of sericin solutions.—Most of the sericin solutions used in this work were prepared by an autoclaving method similar to that described by other investigators.[7, 8, 10] The raw silk was placed in a beaker of water at about 100° C. in the autoclave, the ratio of fibre to water being 1 to 50. Steam was passed into the autoclave until a temperature of 114–115° C. was reached. Approximately five minutes was required for this operation. The temperature was then maintained by addition of more steam for the duration of the treatment. The silk was removed from the

solution, squeezed, and immediately rinsed in one 500-ml portion of water at 90° C. As much liquid as possible was squeezed from the silk and combined with the rinse solution and the solution obtained after autoclaving. The combined solutions were then rapidly cooled to room temperature in a water bath.

3. Fractionation of the sericin.—In earlier work, the fractionation of the sericin in solution was accomplished by the use of alcohol or ammonium sulfate, but in more recent work, most investigators have preferred to use different buffer solutions. It was found necessary, however, to redetermine the pH for maximum precipitation as the values reported in the literature [8, 10] vary from pH 3.6 to 4.1. A preliminary experiment was made on a solution of sericin, prepared by a 30-minute treatment in the autoclave. The solution was brought to room temperature and aliquots of it were immediately adjusted to definite pH values in the range from 3.5 to 4.3 with acetate buffers of constant ionic strength (0.02 *M*). After 15 hours, the precipitated protein was centrifuged off, and the total nitrogen content (a measure of the protein remaining in solution) and the pH of the supernatant liquid were determined. A considerable portion of the protein was precipitated in the pH range used, but maximum precipitation appeared to occur at pH 4.0. In all subsequent fractionation experiments, the solutions were adjusted to this pH and allowed to remain in a refrigerator overnight before removal of the insoluble protein.

The fraction which is insoluble at pH 4 was separated from the remainder of the solution with a centrifuge. The precipitate was thoroughly washed with fresh portions of the acetate buffer, then with alcohol and with ether, and finally dried for four hours in a vacuum oven at 50° C.

The acetate washings were added to the solution remaining after centrifuging and the whole was evaporated to a small volume by passing a stream of air over it at room temperature. The protein in the concentrate was precipitated by addition of the solution to a sufficient volume of alcohol (95%) at about 0° C., to make the final concentration of alcohol 75%. The precipitate was separated from the solution with a centrifuge, washed with alcohol and with ether, and dried in the vacuum oven for four hours at 50° C.

The solution remaining after the separation of the protein which was insoluble in 75% alcohol was combined with the alcohol and ether washings from both sericin fractions, evaporated to dryness on the steam bath, and the weight of the residue determined. The solid material was dissolved in a small amount of water, the solution diluted to 25 ml, and suitable aliquots were taken for nitrogen, tyrosine, and carbohydrate determinations.

4. Designation of the sericin fractions.—The authors do not intend to perpetuate, in future papers, the use of the following terms for the designations of the sericin fractions. These terms, which were adopted by previous investigators, are used in this paper merely for convenience and to avoid further confusion. Sericin B is the fraction of the protein which is insoluble at pH 4. The fraction which is soluble at pH 4 but insoluble in a 75% solution of alcohol is called sericin A. In the present investigation, a small fraction soluble in 75% solution of alcohol was also found. For convenience, this material is referred to as sericin D, although in a series arranged in descending order with regard to solubility, it should precede sericin A. The existence of another fraction, sericin C, has been reported and described by Mosher [8] as extremely insoluble.

Results and Discussion

The effects on dewaxed silk of varying the duration of the autoclave treatment are shown in Table 2 and Fig. 1. About 80% of the total seri-

TABLE 2

Effect of duration of autoclaving on the yields of Sericin A, B and D.

Duration of Autoclaving	Loss in wt. of dewaxed silk	Sericin B	Sericin A	Sericin D	Total extracted sericin accounted for
min.	%	%	%	%	%
5	12.6	97.1	2.7	Trace	99.8
20	18.9	93.3	3.7	1.1	98.1
60	21.1	77.5	21.2	1.3	100.0
180	22.9	18.7	77.4	3.8	99.9

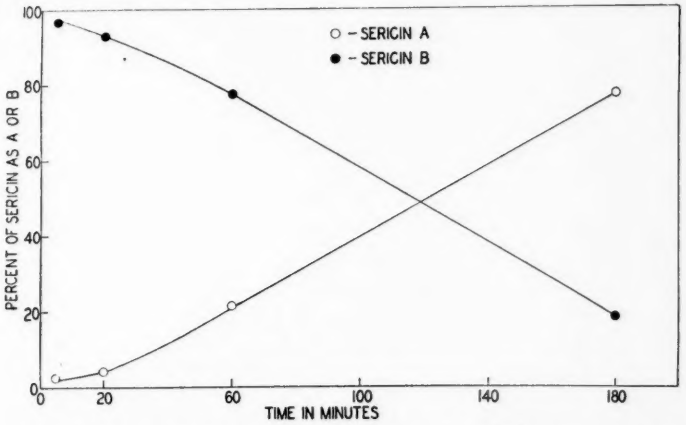

Fig. 1. Effect of duration of autoclaving on the yields of sericin A and B.

cin of the silk is removed in as little time as 20 minutes; practically complete removal is accomplished in approximately one hour. The yields of sericins A and B are seen to vary considerably with the duration of autoclaving. Of the total sericin removed during treatment of dewaxed silk for five minutes, more than 97% was in the form of sericin B. The yield of this fraction decreased, however, as the duration of the autoclave treatment was increased until, after three hours, only 18.7% of the total sericin was recovered in this form. On the other hand, the very low yield of 2.7% of sericin A, obtained during the five-minute treatment, was increased to 77.4% by three hours in the autoclave. Only a small amount of sericin D was present. As is shown in the last column, practically all of the sericin in solution was accounted for.

The data clearly show that sericin A is a decomposition product of the naturally occurring sericin, and is formed during the autoclave treatment. If, however, fraction A were present in the native raw silk, it would be expected that it would be more rapidly removed, because of its high solubility. Actually, the sericin samples obtained in the shortest times of autoclaving (5 to 20 minutes) were practically entirely in the form of sericin B.

Further evidence supporting the conclusion that the fractions of sericin result from decomposition produced during autoclaving of the fibres is found in the analytical data of the different fractions as shown in Table 3.

TABLE 3

Nitrogen and tyrosine contents of the sericin fractions obtained from dewaxed silk during autoclaving for different lengths of time at 115° C.

Duration of autoclaving	Sericin B				Sericin A			
	Yield	Total nitrogen	Tyrosine	Amino nitrogen	Yield	Total nitrogen	Tyrosine	Amino nitrogen
min.	%	%	%	%	%	%	%	%
5	97.1	16.87	6.2	0.32	2.7	13.94	Trace	—
20	93.3	17.00	6.5	—	3.7	15.68	2.5	—
60	77.5	17.23	6.5	—	21.2	16.44	5.1	—
180	18.7	16.44	5.4	0.45	77.4	16.67	6.5	0.49

The data show that sericins A and B as obtained under these conditions are not definite chemical entities but are substances whose chemical compositions vary with the length of the autoclave treatment. A comparison of these data with the calculated total and amino-nitrogen, and tyrosine contents of sericin in dewaxed silk (Table 1) indicates that the sericin B fraction, obtained from silk during autoclaving for only five minutes, is probably very similar to the undegraded sericin. This similarity and the fact that more than 97% of the sericin removed in this time is sericin B strongly suggest that all of the sericin in raw silk is present in one form.

Since the bulk of the sericin is removed in a relatively short time, and practically entirely in the form of sericin B, the increasing yields of sericin A must result principally from the decomposition of the sericin B after the latter has been removed from the silk. This decomposition appears to proceed fairly rapidly (Fig. 1).

The increase in the yield of the very soluble fraction, sericin D, with increased time of autoclaving, as shown in Table 4, is indicative of even more extreme decomposition of the sericin. The chief interest in this fraction is found in its relatively high carbohydrate and amino-sugar contents. The samples obtained after 20 minutes contain about three times as much of these substances as the original sericin. It should be noted, however, that although there is a fourfold increase in yield of sericin D when the duration of the autoclave treatment is extended from 20 to 180 minutes, there is only a comparatively small increase in the total yields of amino sugar and carbohydrate. In other words, the first of these very

TABLE 4

Effect of the duration of the autoclave treatment on the yield of sericin D.

Duration of autoclave treatment	Yield [a] of sericin D	Carbohydrate (as glucose)	Amino sugar (as glucosamine)
min.	mg.	mg.	mg.
20	102	4.7	4.0
60	134	6.4	6.1
180	432	7.4	6.9

[a] Yield from 50 grams of dewaxed silk.

soluble decomposition products is relatively rich in these substances, but the subsequent fractions of the sericin contain appreciably lower amounts.

The data in Table 3 also show that the conversion of sericin B to A is accompanied by an increase in amino-nitrogen content, sufficient to account for an appreciable amount of hydrolysis. Additional evidence that hydrolytic decomposition occurs during treatment of sericin with boiling water was obtained in the following experiment: A sample of dewaxed silk was placed in boiling water and aliquots of the resulting sericin solution were removed at different time intervals for the determination of total and amino nitrogen. The results are presented in Fig. 2, and show that hydrolysis of the sericin proceeds at an appreciable and fairly constant rate.

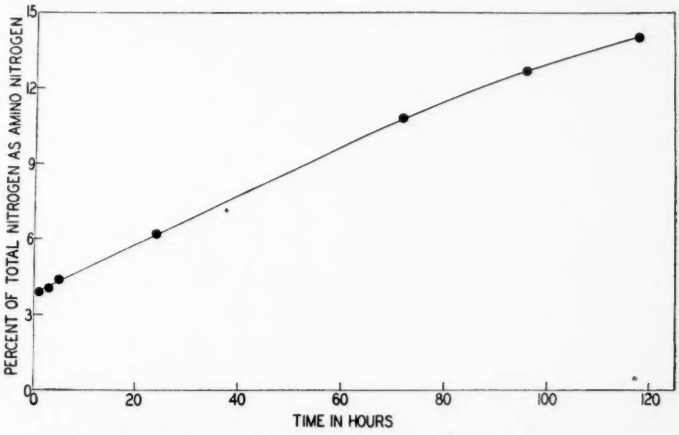

Fig. 2. Rate of increase of the amino-nitrogen content of a sericin solution during prolonged treatment at 100° C.

No attempt has been made to isolate the sericin C fraction because, as shown above, none of the isolated fractions has any particular significance as regards the sericin as it exists in the raw silk.

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(*Continued from Page 220*)

Dr. Albert C. Walker, of Bell Telephone Laboratories and chairman of the Administrative Committee for the Institute's research on textile drying, and Wright Bolton, general superintendent, Rayon Fabrics Div., Pacific Mills, who was chairman of the Administrative Committee for the Institute's completed research on the warp sizing of filament rayon, were the speakers at the March meeting of the American Association of Textile Technologists. Dr. Walker's subject was "The Scientific Approach to Textile Problems," and emphasized the importance of correct statistical procedure, and was illustrated by methods utilized in the Institute's textile drying research and by certain of its results. Mr. Bolton answered the question "Of What Use is Research in Industry?" by citing certain results of the warp sizing research with which he was associated. He admitted that additional research on this subject is needed, and mentioned as one of the problems elimination of adhesion of sized warps to drying surfaces.

* * *

Nathaniel McL. Sage, who is widely known in business and industry throughout the country as Placement Officer of the Massachusetts Institute of Technology, has been appointed Director of the Institute's Division of Industrial Co-operation. He has been acting head of the division since the death last September of Prof. Charles L. Norton, who for many years had charge of Technology's research services in the solution of industrial problems. Mr. Sage is experienced in industrial and business management, having served as production superintendent, sales manager, vice-president, and president in a number of companies in the fields of building construction, shipbuilding, manufacturing, and advertising.

Combination of Wool Protein with Acid and Base: Hydrochloric Acid and Potassium Hydroxide*

By JACINTO STEINHARDT and MILTON HARRIS †

A Textile Foundation Publication

(Concluded from the March issue)

III. Results and Discussion

1. Combination with Hydrochloric Acid

Measurements of the combination of wool with hydrochloric acid as a function of pH at 0° C are given in Table 1, in which each section, except the first, summarizes data obtained at a different constant ionic strength. In the first section each measurement represents a different ionic strength since no salt was added. Data obtained both by titration of acid and of chloride are given. As was to be expected from considerations of electrical neutrality, the values in the two columns agree very closely. This agreement shows that the small amount of alkaline ash in the material used in most of the experiments neutralizes only negligible amounts of acid. In those cases in which much ash was known to be present, the agreement demonstrates the adequacy of the corrections applied for the effect of this ash.‡

The measurements of acid bound (Table 1) are represented graphically in Fig. 2, in which the continuous curves serve to differentiate the sets of points from one another. All of the other curves shown are distinguished from the "no-salt" curve (at the extreme left of the figure) by their smaller slopes. When compared at a point well above the base line, as, for example, at the points at which half the maximum acid-binding capacity is found, the slopes of all of them are very nearly equal. Near the base line the slopes vary as the curves converge and finally cross.§ The addition of even small amounts of salt suffices to produce this difference: thus, when compared at 0.05 millimole of acid bound per gram, the point on the curve obtained with a total ion concentration of only 0.005 is shifted with respect to a corresponding point on the no-salt curve by about 1.3 pH units. The

* Part of the material in the present paper was presented at the meeting of the American Society of Biological Chemists at Toronto, Canada, in April, 1939.

† Research Associates at the National Bureau of Standards representing the Textile Foundation.

‡ When alkaline ash is combined with wool, the chloride disappearing from solution rather than the decrease in titratable acidity is a measure of the acid which would be taken up by ash-free wool. Thus, curves of chloride bound as a function of pH, although of lower accuracy, require no adjustments for the presence of ash.

§ The positions of the curves are reversed on the alkaline side of the point of zero combination and again tend to become parallel.

TABLE 1

Combination of Wool with HCl at 0°

(*a*) *No Added Salt*

pH	Acid Bound millimoles per g	Chloride Bound millimoles per g
*0.447	0.868	——
0.635	0.838	——
*0.792	0.836	0.810
0.813	0.805	0.804
*0.814	0.829	0.836
*0.918	0.813	——
*1.087	0.762	0.771
1.125	0.789	0.736
1.470	0.768	0.754
*1.663	0.676	0.694
1.711	0.652	0.654
*1.741	0.631	0.635
1.931	0.574	0.585
*2.061	0.510	0.515
2.228	0.445	0.440
*2.340	0.385	0.399
2.451	0.348	0.353
2.726	0.251	0.261
3.039	0.166	0.169
3.272	0.114	0.113
3.620	0.067	0.071
3.844	0.045	——
4.198	0.027	0.023
4.414	0.017	0.023
4.740	0.012	0.018
5.145	0.004	0.009

(*b*) *Ionic Strength 0.005*

2.340	0.385	0.399
2.681	0.314	0.324
2.980	0.264	0.263
3.469	0.187	0.193
3.778	0.146	0.143
4.130	0.113	——
4.403	0.085	0.088
4.701	0.058	0.073
5.108	0.045	0.046
5.236	0.035	0.039
5.670	0.022	0.024
5.769	0.021	0.019
5.96	0.009	——
6.5	0.000	——

(*c*) *Ionic Strength 0.01*

pH	Acid Bound millimoles per g	Chloride Bound millimoles per g
2.061	0.510	0.515
2.442	0.427	0.427
2.705	0.369	0.368
2.982	0.312	0.312
3.326	0.250	0.266
3.593	0.209	0.221
3.856	0.167	0.167
4.412	0.113	0.118
4.652	0.089	0.095
5.072	0.061	0.079
5.317	0.050	0.059
5.649	0.032	0.043
5.98	0.017	0.021
6.41	0.008	——
6.5	0.000	——

(*d*) *Ionic Strength 0.02*

1.741	0.631	0.635
1.950	0.591	0.621
2.265	0.525	0.525
2.675	0.429	0.429
3.017	0.365	0.366
3.368	0.289	0.295
3.668	0.240	0.238
3.945	0.202	0.204
4.563	0.121	0.118
5.048	0.074	0.080
5.622	0.042	0.047
6.4	0.000	——

(*e*) *Ionic Strength 0.04*

1.663	0.676	0.694
1.830	0.668	0.675
1.925	0.650	0.678
2.152	0.605	0.616
2.620	0.505	0.494
2.639	0.500	0.494
3.016	0.406	0.400
3.294	0.357	0.382

* No-Salt data from experiments at constant ionic-strengths in other columns.

TABLE 1—*Continued*

(*e*) *Ionic Strength 0.04*—Continued		
pH	Acid Bound millimoles per g	Chloride Bound millimoles per g
3.628	0.280	0.319
4.035	0.229	0.222
4.377	0.171	0.193
4.650	0.146	0.140
5.080	0.102	0.102
5.283	0.082	0.082
5.40	0.064	0.063
6.3	0.000	−0.011
(*f*) *Ionic Strength 0.1*		
1.087	0.762	0.771
1.201	0.789	0.794
1.380	0.767	0.776
1.678	0.745	0.740
1.988	0.704	——
2.269	0.664	0.680
2.535	0.603	——
2.810	0.538	0.510
3.206	0.446	——
3.650	0.357	——
4.210	0.250	——
4.617	0.176	0.195
5.032	0.122	——
5.473	0.075	——
5.867	0.037	——
6.15	0.016	——
6.3	0.008	——
6.4	0.003	——
6.5	0.000	——
(*g*) *Ionic Strength 0.2*		
0.792	0.836	0.810
†0.814	0.829	0.836

(*g*) *Ionic Strength 0.2*—Continued		
pH	Acid Bound millimoles per g	Chloride Bound millimoles per g
††0.918	0.813	——
1.100	0.799	0.788
††1.130	0.798	0.828
°1.400	0.789	——
1.409	0.788	0.773
††1.433	0.774	0.780
1.707	0.770	0.756
††1.751	0.753	0.775
†1.982	0.730	0.730
2.038	0.740	0.756
††2.061	0.702	0.759
2.364	0.701	0.712
††2.378	0.670	——
2.708	0.641	——
††2.744	0.595	——
°2.790	0.594	——
3.172	0.535	0.591
††3.273	0.487	——
†3.571	0.435	——
3.670	0.419	0.460
††3.825	0.372	——
4.082	0.320	0.294
†4.359	0.279	0.300
4.662	0.224	0.198
††4.855	0.177	——
5.015	0.168	——
5.246	0.131	0.120
††5.400	0.112	——
5.528	0.099	0.085
††5.564	0.067	——
5.670	0.078	——
5.887	0.054	——
††5.94	0.030	——
6.14	0.023	——
††6.3	0.002	——
6.5	0.002	——
††6.7	−0.027	——
6.97	−0.048	——
††7.0	−0.041	——

†, ††, ° Supplementary control determinations on batches containing alkaline ash. These data are corrected for differences in ash as explained in the text.

magnitude of this effect may be made clearer by comparing the amounts of acid bound at the same pH. In the absence of salt, only a little more than 0.01 millimole of acid per gram is bound at pH 4.6, but the addition of salt, sufficient to bring the concentration of chloride to 0.005 *M*, increases this figure almost sixfold. At pH 5 and above, this factor is even larger. Conversely, as the part of the total ionic strength which is contributed by salt

TABLE 1—*Continued*

(*h*) *Ionic Strength 0.5*		(*i*) *Ionic Strength 1.0*Δ	
pH	Acid Bound millimoles per g	pH	Acid Bound millimoles per g
0.447	0.868	0.578	0.920
0.832	0.838	0.840	0.890
1.130	0.850	1.1[illegible]	0.852
1.438	0.799	1.445	0.840
1.745	0.784	1.743	0.794
2.048	0.781	2.062	0.777
2.780	0.687	3.074	0.652
3.750	0.471	4.258	0.403
3.910	0.432	4.334	0.395
4.304	0.330	4.768	0.288
4.887	0.228	5.342	0.208
5.211	0.164	5.651	0.119
5.472	0.112	5.908	0.065
5.870	0.068	6.4	0.013
6.10	0.034	6.7	−0.015
6.5	0.002	7.0	−0.048

Δ Data in this column corrected for alkaline ash of wool used.

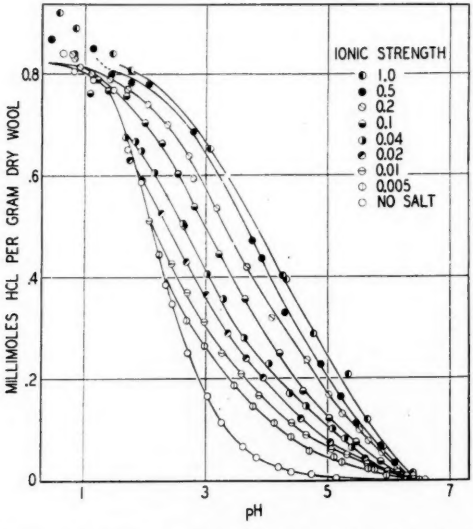

Fig. 2. The combination of acid by wool as a function of pH and ionic strength at 0°. (To avoid crowding the figure, only a single set of the experimental values obtained at an ionic strength of 0.2 is included. The smooth curves serve merely to distinguish the sets of data from one another.)

dimin ·s, the factor becomes smaller, and each curve finally terminates at its int· tion with the curve obtained without salt.

A s· le regularity relates the curves obtained with different total ionic strengths: the distance (with respect to pH) between any two adjacent curves, taken for convenience at the point of half of the maximum combination with ·id, is only slightly less than the logarithm of the ratio of the ion concent· ons which the curves represent. This implies a close approach to a dire ·to· ·ometric relationship of the acid bound by wool to the concentration of el· ion as well as to the concentration of hydrogen ion: thus, each time the chl·de concentration is doubled, the curves are shifted to pH values approximately 0.30 unit higher than those at the lower ionic strength. As shown in Fig. 3, this direct relation is approximated

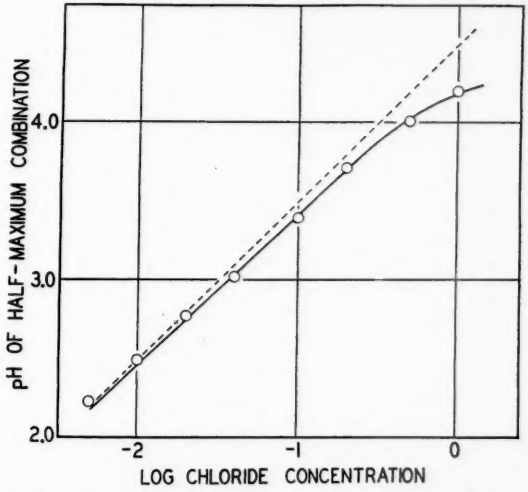

Fig. 3. The dependence of the pH of half-maximal combination with acid on the level at which the chloride concentration is held constant. The broken line represents a direct stoichiometric relation.

very closely over the forty-fold range of chloride concentrations between 0.005 and 0.200 *M*. Above this range the dependence on ionic strength diminishes: it appears that the curves may approach a limiting position with respect to the pH axis, and that this limit may not be far beyond the position of the curve at 1.0 *M* ionic strength. It is significant that the pH for half maximal combination (4.2) which characterizes the position of the curve at 1.0 *M* chloride is practically identical with the mid-point of the first S-shaped portion of the titration curves of soluble proteins measured at the same salt concentration.

The remarkably regular dependence of the positions of the curves on the total concentration of chloride ions may be interpreted as implying a certain degree of interchangeability of the concentrations of acid and salt or of hydrogen and chloride ions as factors limiting the amounts of acid bound.

The function which describes the amount of acid bound must involve two independent variables, and its dependence on each of these variables must possess a degree of similarity. Thus if, instead of plotting the amount of acid bound against pH, it were plotted against the negative logarithm of the total chloride concentration at a number of constant concentrations of acid, a group of curves would be obtained related to one another very much as the curves in Fig. 2. Several earlier studies on *soluble* proteins [4, 10] have shown the existence of much smaller effects of salt on the positions and shapes of their acid-titration curves. These effects are only slightly larger than those which characterize the common buffers, and which are explained in terms of the modern electrical-interaction theory of solutions. They cannot be compared to the much larger and nearly stoichiometric dependence which is found with wool in the range of low ionic strengths. The significance of this large and interchangeable dependence of acid and salt on acid combination is discussed in section IV of this paper.

Since the curves of acid combination as a function of pH represent the reaction of hydrogen ions with carboxylate ions (see footnote on Page 184) and since the dissociation constants of the conjugate carboxylic acids have only a slight dependence upon temperature (between 0° C and room temperature) the effect of temperature on these curves should be small. This expectation is completely fulfilled by comparison of the data at 0° already given with the measurements on wool at 25° C summarized in Table 4 and plotted in Figs. 1 and 5.* Comparison of the data obtained in the absence of salt at either temperature with the data of Speakman and Stott,[45] obtained at an intermediate temperature, is therefore not unjustified. The agreement with the data of these investigators is close over the greater part of their range, and is probably within the limits of possible differences in definition of the pH scale in the two investigations. Although different wools were used, there is also close agreement between the values for maximum acid-binding capacity. As shown in Fig. 2, all of the sets of points tend to level off near pH 1 at 0.80 to 0.84 milliequivalent of acid bound per gram.† Speakman obtained a maximum of 0.80 or 0.81 with wool which had been previously extracted with very dilute hydrochloric acid to remove the ash. The agreement of our maximum values with his supports the previous conclusion that the residual 0.10% of ash in the wool used in the present investigation is practically without effect on the measurements. This conclusion is also borne out by the amounts of acid shown to be bound in the absence of salt at pH 4.8, which Speakman considers to be the point of zero combination. This quantity, approximately 0.01 millimole per gram, is therefore the maximum amount which may be attributed to ash present in the wool of the present investigation. The effect of this ash in neutralizing acid may be even smaller, or zero, since Speakman's acid extraction and adjustment to pH 4.8 may have resulted in the combination of so small an amount of acid as 0.01 millimole with his wool. The curves obtained in the

* A closer study of the effects of temperature on combination with acid and base is in progress. These effects are of importance in the application of the low-temperature titration data presented in this paper to such related aspects of wool processing as dyeing and scouring, which usually involve high temperatures.

† The slight differences in the maxima shown by the various curves may represent, in part, residual differences in alkaline ash for which inadequate corrections have been made. It is more likely that they are the result of incorrect allowance for differential absorption of water, salt, and acid when wool unsaturated with water is placed in the various solutions. This absorption will affect only the values calculated for the most acid solutions. It is also possible that in the most acid solutions, the titration of the very weakly basic amide groups is begun, and that the curves are not entirely level below pH 0.7.

presence of salt make plain that pH 4.8 is not the point of zero combination of acid with wool at 0° C. It seems probable that at this temperature the base line is crossed, not only in the presence of salt but in salt-free solutions as well, at pH 6.3–6.5.

2. *Combination with Potassium Hydroxide*

Although fewer measurements of the combination of wool with base have been made, they suffice to show that the relationships between the data on acid combination obtained in the presence and absence of salt, and at different constant ionic strengths, also prevail in the alkaline branches of the wool titration curves. Very little modification of the foregoing description is therefore necessary. The corrected data for base combination at 0° C, at two ionic strengths and in the absence of added salt, are summarized in Table 2. Parallel data for the combination of the fibre with

TABLE 2

Combination of Wool with KOH at 0° *

(*a*) *No Added Salt*		(*b*) *Ionic Strength 0.02*		(*c*) *Ionic Strength 0.20*	
pH	Base Bound millimoles per g	pH	Base Bound millimoles per g	pH	Base Bound millimoles per g
†† 9.45	0.055	8.59	0.047	† 6.95	0.050
††10.01	0.063	10.25	0.095	7.68	0.050
††10.43	0.077	10.62	0.112	8.28	0.093
††10.91	0.094	11.09	0.142	9.84	0.130
11.32	0.105	11.60	0.170	10.83	0.180
11.37	0.097	11.90	0.191	11.63	0.273
11.93	0.128	12.27	0.236	†12.23	0.391
12.17	0.153	12.60	0.262	12.25	0.389
12.46	0.185	12.81	0.316	12.62	0.462
12.72	0.232	13.03	0.348	12.68	0.495
12.88	0.297	13.22	0.397	13.01	0.582
13.12	0.375			†13.11	0.600
°13.22	0.397			13.19	0.635
13.32	0.436			†13.39	0.649
13.35	0.476			††13.82	0.704
13.49	0.565			†††13.82	0.722
††13.65	0.586			†13.85	0.710
13.68	0.590			Δ14.11	0.764
13.85	0.669			††14.13	0.723
††13.85	0.611			†14.16	0.630
14.11	0.764			†††14.17	0.730
††14.13	0.723				
†14.16	0.630				
†††14.17	0.730				
14.29	0.828				
††14.30	0.787				

†, †† Supplementary control determinations on different conditioning batches, and with different periods of equilibration.

††† Control determinations on wool of different ash content.

° Data from column (*b*).

Δ Data from column (*a*).

* The data are corrected for the effects of decomposition and for their content of alkaline ash, as explained in Section II.

potassium ion, obtained by electrodialysis, are omitted from this table; although less accurate than the data for base bound, they are in fair agreement with the values given. In Fig. 4, the data of Table 2 are shown combined with the corresponding sets of measurements for acid combination; the figure thus represents the complete titration curve under these conditions over the entire pH range studied.

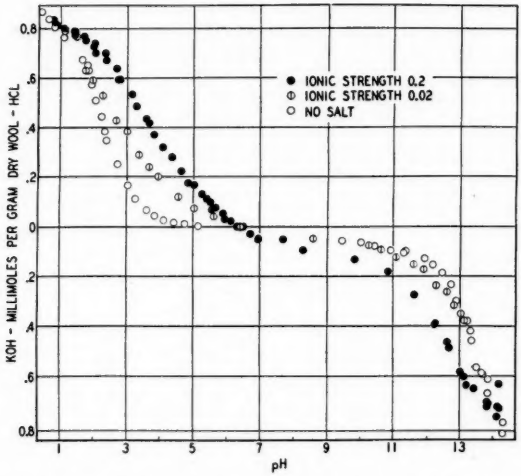

Fig. 4. The combination of wool with hydrochloric acid and with potassium hydroxide as a function of pH. Data are shown obtained in the absence of added salt, and in the presence of two different constant total ionic concentrations.

When the data obtained at constant ionic strengths are so presented in their entirety, the composite curves bear a close resemblance to the titration curves of dissolved proteins. The acid branch crosses the base line without discontinuity and continues downward with progressively more gradual slope until buffering capacity is practically lost over a range of 1 to 2 pH units. Approximately 0.10 millimole of base per gram has been bound at this point. As the pH increases, marked buffering capacity once more appears and large amounts of base are bound in the pH range 11–14. The largest amount bound in the range measured is 0.78 millimole per gram, but there is no indication from the shape of the curves that somewhat larger amounts of base would not be bound at a higher pH. This maximum value is slightly higher than that reported by Harris and Rutherford. The cause of part of this difference has already been given (see Experimental Procedure). Another part may be due to the alkaline ash content of the wool yarn, as pointed out in the earlier work.

Although the alkali titration curve is more complex than that of the acid curve, the shifts produced in its position by salt are exactly analogous to the shifts in the acid curves. Thus, every point on the curve representing measurements at 0.02 *M* is shifted to the alkaline side by almost exactly

1.0 pH unit from the corresponding point at 0.20 *M*. The data obtained without salt are widely separated from the others, especially as the pH for zero combination is approached. The curve representing the data obtained in the absence of salt in both alkaline and acid solutions consists of two steep sections and shows clearly the long central region of about 5 pH units in which the amounts of acid or base bound are very small.

3. Relations to Titration Curves of Soluble Proteins

The occurrence of a large and nearly stoichiometric dependence of the pH coordinate of the titration data for wool on the ionic concentration makes it of some interest to determine whether any of the large number of possible positions of the resulting curves corresponds with the curve which would characterize a similar protein in the dissolved state. It has been shown (Fig. 1) that the acid curves of wool and of a comparable soluble protein, egg albumin, obtained in the total absence of salt, differ very widely. In Fig. 5, data for the same two proteins are compared at a high salt concentration, 0.5 *M*. Above this concentration the positions of the titration curves with respect to the pH axis have a lower degree of dependence on salt concentration.*

The data for wool shown in Figs. 1 and 5 were obtained at 25° C, the temperature used by Cannan, and are summarized in Table 3. The points

TABLE 3

Combination of Wool with Hydrochloric Acid at 25° *

(*a*) *No Added Salt*		(*b*) *Ionic Strength 0.50*	
pH	Acid Bound millimoles per g	pH	Acid Bound millimoles per g
0.638	0.877	0.412	0.877
0.826	0.802	0.839	0.810
1.448	0.687	1.154	0.815
1.710	0.599	1.470	0.824
1.915	0.520	1.774	0.757
2.191	0.402	2.088	0.762
2.406	0.316	2.835	0.636
2.722	0.225	3.772	0.426
3.093	0.143	3.929	0.383
3.370	0.087	4.380	0.281
3.962	0.036	4.852	0.214
4.603	0.014	5.33	0.140
5.257	†−0.013	5.82	0.082
6.38	†−0.026	6.25	0.023
6.82	†−0.035	6.50	0.002
7.28	†−0.042	6.72	†−0.026

* The data are corrected for water uptake by the fiber and the effect of its alkaline ash as explained in Section II.

† Negative values indicate loss of bound acid or combination with hydroxyl ion.

for egg albumin in Fig. 5 represent interpolations at equidistant points along the pH axis between the curves given by Cannan [4] for 0.27 and 0.67 *M* salt. The data for wool at 25° C differ only slightly from those at 0° already described.

* The smaller shifts that occur at salt concentrations above 0.5 *M* are of practically the same magnitude as those which occur with the dissolved protein in the same range of concentrations.

It is clear that the differences between the data for the two proteins, so marked in Fig. 1, have been greatly reduced in Fig. 5. Aside from a slightly more acid position for the curve for wool, discrepancies to which significance may be attached appear only in the region of very slight acid binding. These discrepancies are very small. Some disagreement might be expected in this region owing to small differences between the ratios of imidazole to carboxyl groups in the two proteins. Since the histidine content of both proteins is small, it is very likely that the analytical values reported are not exact.

This comparison shows that proteins of comparable composition with respect to dicarboxylic amino acids and histidine, give closely similar acid-combination curves when they are compared over the same acid range in

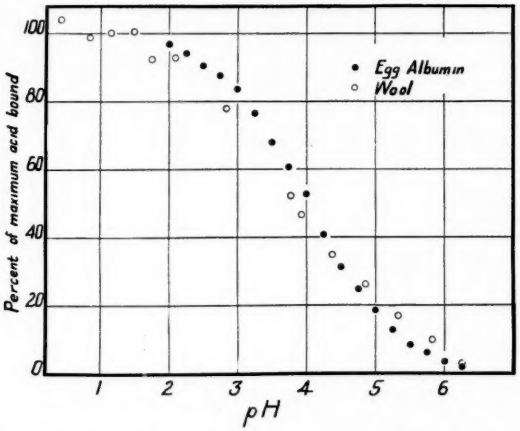

Fig. 5. Comparison of the curves of acid combination of wool and of egg albumin at 25°, in the presence of 0.5 *M* chloride.

solutions containing high concentrations of ions. This result must be taken into account in any explanation offered for the great difference in acid-binding behavior between the same proteins when neutral salts are absent. In itself, the comparison is sufficient to exclude from consideration explanations which appeal to a fundamental difference in configuration of the acidic and basic groups in the two classes of substances. The comparison gains further significance from Cannan's demonstration that the egg albumin curves of Figs. 1 and 5 are very similar to those of polyvalent acids in which all of the dissociating groups have the same intrinsic strength, but in which the negative charges left by the dissociation of each hydrogen ion hinder the dissociation of the remaining groups. The present comparison indicates that Cannan's reasoning must apply to wool to the same degree as to egg albumin. The differences between the titration curves of the two proteins found in the absence of salt must find their explanation in elements of an equilibrium which occurs between two phases.

4. Analysis of the Titration Curves

By analogy with similar analyses of titration curves of soluble proteins [8, 9, 10, 27, 28] it should be possible to identify each portion of the curves for wool at high constant ionic strength with one of the several kinds of dissociating groups contributed by the constituent amino-acid residues. The acid branch is clearly attributable to the back-titrations of the ionized carboxyl groups of glutamic, hydroxyglutamic, and aspartic acids, overlapping in the pH range above 4.5 the combination with acid of the imino groups of histidine. In addition, those carboxyl groups which have not donated their protons to amino and guanidino groups (the excess of carboxyl groups over these groups) must be responsible for part of the unbroken continuation of this S-shaped curve to pH 8; another part is contributed by the removal of protons from those histidine residues which have their imino groups in the charged (acid) form. In the unbuffered region between pH 8 and 10 almost no groups dissociate, but in the buffered section of the curve (pH 11–14) the ϵ-amino groups of lysine are regenerated from their conjugate acid forms by loss of a proton. In addition, the hydroxyl groups of tyrosine (if they are free in wool) become ionized, and at least some of the guanidino groups of arginine, present in their conjugate acid form, give up their protons.

The foregoing partial analysis of the composition of the high ionic strength curves may be rendered more convincing by the following quantitative comparison of its implications with the admittedly incomplete data at present available on the amino-acid composition of wool.

The sum of the acid-binding and base-binding capacities of wool between pH 0.8 and 14.3 is $1.59 \pm .04$ millimoles per gram. Table 4 lists the reported contents of aspartic and glutamic acids, histidine, lysine, arginine, amide nitrogen, and tyrosine. The sum of the acid- and base-binding equivalents, *omitting the tyrosine*, and after subtraction of the amide nitrogen to allow for the part of the dicarboxylic acids present as glutamine and asparagine, is 1.46 millimoles per gram. *With the tyrosine included* it is

TABLE 4

Acidic and Basic Amino-Acids in Wool

	Ref.	Percent	Millimoles per g
1. Aspartic Acid	(46)	7.27	0.545
2. Glutamic Acid	(46)	15.27	1.035
3. Amide nitrogen	(46)	1.37	0.978
1 plus 2 minus 3	—	—	0.602
4. Arginine	(16)	10.2	0.586
5. Lysine	(39)	3.3	0.226
6. Histidine	(50)	0.66	0.044
4 plus 5 plus 6	—	—	0.856
1 plus 2 minus 3 plus 4 plus 5 plus 6		—	1.458
7. Tyrosine	(38)	5.8	0.320

1.78. Both figures are given because the experimental sum falls between them, and because there is a suggestion in certain unpublished data on wool and in published data on some soluble proteins [15, 47] that some or all of the hydroxyl groups of tyrosine in proteins may not be free to combine with base. Another explanation of the small discrepancy is possible: the figures for the carboxylic acids and histidine were obtained by isolation methods and are likely to be low. Should this be the case one may conclude that tyrosine hydroxyl groups are *not* titrated. However, it is not certain that the present measurements give the maximum base-binding capacity, and only part of the arginine may be combined with base at pH 14.3. Should this be true one may conclude that the tyrosine is titrated quantitatively.

It is possible to calculate roughly what the maximum base-binding capacity should be, from the maximum amount of acid which is bound and the pH at which no combination with either acid or base occurs. Since the latter falls in the titration range of histidine, which is present in small amount, it appears that in the uncombined state of the protein practically all the carboxyl groups have donated their hydrogen ions to basic groups. Thus the sum of the basic groups (from lysine and arginine) must be equal to the sum of the carboxyl groups (from glutamic, hydroxyglutamic, and aspartic acids) within a margin of uncertainty which is smaller than the small content of histidine. The maximum base-binding capacity, *excluding tyrosine*, should therefore correspond roughly with the maximum acid-binding capacity,—which may be taken as 0.82. The sum of the two should not be far from $2 \times 0.82 = 1.64$, a figure close to 1.59, the value found. It would be necessary to assume that about half the arginine is still not titrated at pH 14.3 in order to make room for the titration of all the tyrosine. This would increase the maximum amount of base bound at higher alkalinities to about 1.18, far above the figure found at pH 14.3. The balance of probability therefore favors the conclusion that in the unhydrolyzed wool the hydroxyl groups of tyrosine are not free to combine with base, and therefore contribute no part of the large buffering effect at pH 11–14.

This conclusion entails the plausible assumption that some or all of the analytical data are low. Since the sum of the arginine and lysine listed in the table is 0.82 millimole per gram, in good agreement with the capacity of wool to bind acid, the largest part of the discrepancy must be sought in the values for the dicarboxylic acids and amide nitrogen, in both of which the potentialities for error have long been recognized. The relatively large amount of acid plus base combined between pH 6 and 8 (about 0.13 millimole) suggests that the histidine figure in Table 3 may also be low, since only a small part of the combination in this range may be attributed to carboxyl groups. However, an increase in the estimated histidine content will not greatly affect the close agreement of the experimentally determined sum of acid- plus base-binding capacity with the sum calculated from the acid-binding capacity alone, since only an indeterminate part of the histidine content contributes to the curve of acid combination, the balance being responsible for a part of the base combined at higher pH.

This analysis of the structure of the titration curve of wool differs in at least one significant respect from the interpretation offered by MacMahon and Speakman.[36] These authors regard the step on the curve which represents the base bound in salt-free solutions, between the pH at zero combination and the relatively unbuffered section at pH 8–10, as caused by the titra-

tion of sulfhydryl groups which are present in wool that has suffered partial decomposition. In the present investigation on undamaged wool, this step on the curve of base-combination also appears; in the curves obtained in the presence of salt it clearly represents a continuation of the first S-shaped branch of the titration curve which begins its downward course near pH 1, and which has been accounted for above as an expression of the partially overlapping titration of carboxyl and imino groups. It seems unlikely that sulfhydryl groups, which are extremely weak acids, would be appreciably titrated in this range of pH. The formation of strongly acid groups by exposure to light may result in a shift of the pH at zero combination to lower values. This would have the effect of increasing the height of the alkaline step, which Speakman attributed to sulfhydryl.

IV. Theory of the Combination with Acid *

1. The Combination of Insoluble Ampholytes With the Anions of Acids

It has been shown in a previous section (III–1) that the acid bound by wool is a function of the concentration of salt as well as of the concentration of hydrogen ions. Furthermore, the way in which the total anion concentration (from acid plus salt) participates in any equation defining the amounts of acid bound under various conditions must be in some measure analogous to the manner of participation of the hydrogen ion. When it is considered that practically equivalent quantities of hydrogen and chloride ions must be combined, dissolved, or adsorbed by the fibre, it is evident that the extent to which one of these ions may be taken up depends in part on the simultaneous availability of ions of the opposite sign.

Restrictions of the latter kind in two-phase acid-base equilibria have long been known. Cases involving two sharply delimited phases, separated by a membrane which is impermeable to one or more of the ions present, have been treated thermodynamically by Donnan.[12, 13] Application of the Donnan equations to the present case would involve elements of arbitrariness in the choice of volumes, concentrations, concentration-scale (because of the high concentration of dissolved substances), the distinction between acid bound by protein and acid merely dissolved by the medium present in the fibre phase, and in the allocation of the phase-boundary. It will be shown later that with such an arbitrary choice permitted, a good approximation to certain features of the data already described could be made. In other respects the approximation is less successful, and leads to consequences which appear to be incompatible with the comparison made above between data for wool and for soluble proteins. For these reasons, and because of the nearly complete interchangeability of hydrogen and chloride ions suggested by our results in acid solutions, it has seemed preferable to treat the restriction on the combination of wool with hydrogen ions more simply on the basis of three easily stated assumptions:

(1) *The fibre protein combines with chloride ions as well as with hydrogen ions, and the combination of both is subject to the law of mass action,*

* The acid branch of the titration curve has been chosen for discussion because it is composed of fewer distinct components. The treatment here proposed should be applicable, with suitable modifications, to the alkali branch as well.

*or to the Langmuir adsorption law.** This assumption may be thought of as implying the formation of a partially dissociated linkage between RNH_3^+ groups and Cl^- ions. Alternatively, the positively charged acid fibre might be thought of as forming a unimolecular adsorption layer of chloride ions. However, the observation that acid-dye anions permeate a wool fibre with a high degree of uniformity when time for full penetration is allowed shows that if the latter view be taken, adsorption does not occur merely on the outside of the fibre. The existence of stoichiometrical relations in the combination of acid and base by the wool also shows that the adsorption must occur on every molecule in the fibre.

(2) *No recognition need be taken of differences in hydrogen-ion concentrations inside and outside the fibre.* This may signify either that these concentrations are identical, or that they are related to one another in a way which is practically independent of the presence of other ions. The assumption appears to be incompatible with the conventional application of the Donnan treatment to two-phase systems. Nevertheless, it represents a reasonable approximation, if postulate 1 given above is accepted: the existence of partially undissociated protein-chloride combinations would greatly minimize the differences predicted by the Donnan equations for the case of the combination of hydrogen ions alone. Since pH differences are the essential feature of the usual application of the Donnan equilibrium to fibre problems, disregard of this necessarily complicated and, in the present case, arbitrary treatment requires no further *a priori* justification.

Alternatively, postulate 1 may be regarded as a purely empirical way of evading explicit treatment of pH differences brought about by combination of the fibre protein with hydrogen ions alone. As will be shown later, both methods of calculation lead to very similar descriptions of a large part of the experimental phenomena, and a final choice between them can only be made on the basis of a wider field of observation, including comparisons with similar results with soluble proteins and with other insoluble materials, and the effects of other experimental variables which are still under investigation. In the meantime, the present treatment possesses a great advantage in simplicity of calculation.

(3) *The variation of activity-coefficients in the fibre phase may be disregarded.* This is the only procedure possible when the system is not accissible to direct measurement by independent means. The postulate is required only if the law of mass action rather than the Langmuir adsorption equation is used.

It is implied in postulate 1 that an equilibrium,

$$W^{\pm}Cl^- \rightleftharpoons W^{\pm} + Cl^- \qquad (1)$$

in which $W^{\pm}$ represents wool in the uncombined state, occurs in addition to

* The assumption that the mass-action law may be applied implies that the fibre is a dispersed phase. In this case, the fibre must be thought of as a solid solution or as a solution of protein in imbibed water. If, on the other hand, the process of combination is one of adsorption, use of the Langmuir equation to describe it implies chemisorption at definite unsaturated points throughout the fibre; these points may be identified with the acidic and basic groups. Neither alternative involves new assumptions; the validity of one or the other is implied by the familiar experimental fact that the curves of acid combination by wool immersed in water are continuous and free of singular points. Derivations based either on the law of mass action or on the Langmuir adsorption equations necessarily lead to the same result.

The present treatment makes no assumption that the dispersed wool protein is a single chemical individual.

the more familiar acid-base equilibrium which may be written

$$WHCl \rightleftharpoons WCl^- + H^+ \tag{2}$$

If these are the only two equilibria which can occur and if, for simplicity, wool is regarded as a divalent ampholyte, *i.e.*, capable of combining a single equivalent of acid or a single equivalent of base, and two thermodynamic dissociation constants K_A' and K_H' are assigned to the equilibria (1) and (2) listed above, the law of mass action (plus postulate 3 or the Langmuir adsorption law) permits us to write:

$$\frac{[WHCl]}{[WHCl] + [WCl^-] + [W^\pm]} = \frac{1}{1 + \frac{K_H'}{a_H}\left(1 + \frac{K_A'}{a_{Cl}}\right)} \tag{3}$$

The bracketed quantities represent concentrations, a_H and a_{Cl} the activities of hydrogen and chloride ions respectively, and the left hand member represents the fraction of the total wool combined with acid.

The resemblance of eq. 3 to the familiar expression for the ionization of a dibasic acid is apparent. If account is also taken of the hydrogen ions removed from the external solution by absorption in the fibre in an amount equivalent to the negative charge contributed by combined chloride ions, the ratio of acid taken up to total wool becomes:

$$\frac{[WHCl] + [WCl^-]}{[WHCl] + [WCl^-] + [W^\pm]} = \frac{1}{1 + \frac{K_H'K_A'}{a_{Cl}(a_H + K_H')}} \tag{3'}$$

Obviously the successive stages of combination might be formulated with equal *a priori* validity in the alternative equilibria:

$$WH^+ \rightleftharpoons W^\pm + H^+ \tag{4}$$

$$WHCl \rightleftharpoons WH^+ + Cl^- \tag{5}$$

to which the dissociation constants K_H and K_A may be successively assigned. The corresponding form of eq. 3 is then

$$\frac{[WHCl]}{[WHCl] + [WH^+] + [W^\pm]} = \frac{1}{1 + \frac{K_A}{a_{Cl}}\left(1 + \frac{K_H}{a_H}\right)} \tag{6}$$

and the corresponding form of eq. 3′ which represents more closely the measured quantities, is

$$\frac{[WHCl] + [WH^+]}{[WHCl] + [WH^+] + [W^\pm]} = \frac{1}{1 + \frac{K_HK_A}{a_H(a_{Cl} + K_A)}} \tag{6'}$$

The four dissociation constants which appear in these equations are obviously interrelated as follows:

$$K_AK_H = K_A'K_H'$$

Equations 3′ and 6′ differ from one another by the omission of different single terms in a complete expression for the sum of all the ionic states of the wool. This omission leads them to describe quite different relations

between the hydrogen-ion and chloride-ion concentrations at which equal amounts of acid are taken up. Since there is no compelling reason for choosing between them, it is necessary to take both sets of equilibria into account in deriving the most general expression for the fraction of the maximum amount of acid bound as a function of a_H and a_{Cl}. This may be done in two ways, according to whether $[WH^+]$ is larger or smaller than $[WCl^-]$, since only the larger one of these two terms must be included in the numerator of the left-hand fraction, which expresses the part of the wool which binds acid. When $[WH^+]$ is the larger, the positive charge on the fibre is partly neutralized by the smaller term $[WCl^-]$ and partly by chloride ions in an adsorption layer.* Within the range of pH, and salt concentrations to which attention is here confined, and with any assignment of physically reasonable values to K_H' and K_A', $[WH^+]$ will be larger than $[WCl^-]$ and should therefore be chosen for inclusion in the numerator. This choice, implying $K_H \ll K_A'$, leads to the relation:

$$\frac{[WHCl] + [WH^+]}{[WHCl] + [WH^+] + [WCl^-] + [W^\pm]} = \frac{1}{1 + \frac{K_H'}{a_H}\left(\frac{a_{Cl} + K_A'}{a_{Cl} + K_A}\right)} \quad (7)$$

The right-hand member of eq. 7, like that of eq. 3, which it closely resembles, differs from the expression for the dissociation residue of a monobasic acid only by the presence of the term in parenthesis. In the presence of a constant concentration of chloride ions this term is constant. Under these conditions the amount of undissociated acid varies with pH exactly as in the case of a monobasic acid, but the apparent strength of the acid (the position of the curve on the pH axis) varies with the magnitude of the bracketed term, which in turn depends on the concentration of chloride ions. With high anion concentrations the term in parenthesis approaches a limiting value of unity, and the dependence of the acid bound at any given pH on further increases in the anion concentration disappears. Thus, the limiting position of the titration curve is determined solely by K_H' and should correspond with the position of the titration curve of a similar *dissolved* acid. It has already been shown that these properties of eq. 7 correspond to experimental facts.†

The quantitative dependence of the positions of the titration curves described by eq. 7 on the level at which the anion concentration is held constant may be demonstrated by determining the pH for half-maximal combination as a function of the anion concentration. This may be done by equating the right-hand member of eq. 7 to 0.5. The resulting relation is:

$$pH_{\frac{1}{2}} = pK_H' + \log\left(\frac{a_{Cl} + K_A}{a_{Cl} + K_A'}\right) \quad (8)$$

* With dye anions of high affinity for wool fibres, such as those used in substantive dyeing, it would be necessary to substitute in the numerator a term analogous to $[WCl^-]$ in place of $[WH^+]$. When more than one kind of cation is present, however (in the presence of salt), this simple substitution does not suffice. The considerably modified relations which are applicable to cases in which $K_A' < K_H$ are beyond the scope of the present paper.

† Thus, it is K_H' rather than K_H which corresponds to the dissociation constant of the acid in solution. This seems to imply that (in dilute solutions) K_H''s as little dependent on the nature of the anion as K_H. If this is true, the absolute values of K_A and K_A' can depend on the nature of the anion, but the ratio K_A/K_A' cannot. The conclusion is a reasonable one if the difference between K_A and K_A' or K_H and K_H' is attributed almost entirely to an electrostatic effect due to a single charge.

In addition to the relation $K_H \ll K_A'$ already discussed, electrostatic considerations obviously require that $K_A' > K_A$ (and $K_H > K_H'$). Thus, in the range $K_A' \gg a_{Cl} \gg K_A$, the logarithmic term approaches $\log \frac{a_{Cl}}{K_A'}$, and the pH for half-maximal combination, which characterizes the position of the entire acid-combination curve, shows a close approximation to direct dependence on the logarithm of the concentration of chloride ions. This range of direct dependence extends down to the lowest possible values of a_{Cl} (equal concentrations of hydrogen and chloride ions). The upper limit of this range is determined by K_A' which determines the concentration of anions at which a limiting position of the curve is approached.

The properties of eq. 7 are illustrated in Fig. 6 which shows the theoretical curves of acid-combination with respect to pH at several different values of $\frac{K_A'}{a_{Cl}}$. For purposes of calculation K_A has been taken as vanishingly small, since $K_A' \gg K_A$. It is noteworthy that the assignment of an infinitely small value to K_A would make the right-hand members of eq. 7 and 3 identical.

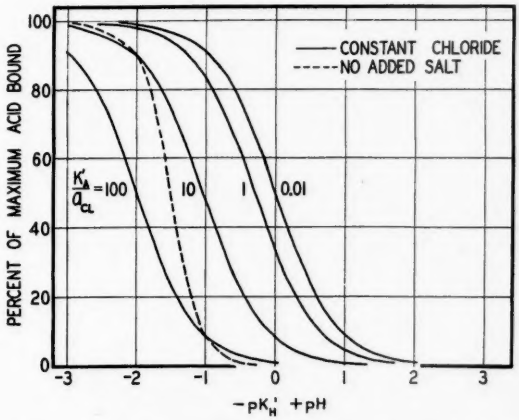

Fig. 6. Theoretical curves of acid-combination described by equations 7 and 7'. The effect of variations in ionic strength is demonstrated by representation of curves for four different values of K'_A/a_{Cl}.

It is clear that the positions of the curves are determined by $\frac{K_A'}{a_{Cl}}$, although their shapes are independent of this ratio. The dependence of the positions on $\log \frac{K_A'}{a_{Cl}}$ is at first linear, but becomes less marked as the ratio diminishes; finally, at very low values of the fraction (a_{Cl} large), the positions of curves approach a limit, determined by K_H'. By utilizing eq. 8, K_A' may be roughly evaluated from the pH differences at the midpoints of curves at two or more different salt concentrations sufficiently high to be beyond the region of simple stoichiometric dependence.

In solutions containing no added salt, a_{Cl} is not constant but equal to a_H. Equation 7 then becomes

$$\frac{[WHCl] + [WH^+]}{[WHCl] + [WH^+] + [WCl^-] + [W^\pm]} = \frac{1}{1 + \frac{K_H'}{a_H}\left(\frac{a_H + K_A'}{a_H + K_A}\right)} \qquad (7')$$

Since K_A' has already been assumed to be large, and K_A very small, there is a wide range of values of a_H in which the bracketed expression reduces to $\frac{K_A'}{a_H}$. The curve in the absence of salt is then described, up to moderately high acidities and high degree of combination, by the relation

$$\text{Fraction of maximum acid bound} \doteq \frac{1}{1 + \frac{K_H'K_A'}{a_H^2}} \qquad (7'')$$

which is entirely consistent with the approximate description mentioned earlier: that the curve for the case of no added salt could be related to the curves at constant ionic strength by substitutions of $[H^+]^2$ for $[H^+]$ in functions describing the latter. The curve in Fig. 6 labelled *no added salt* is drawn to represent eq. 7'. K_A' has been taken to be 1000 K_H' (approximately 0.1) and K_A is considered negligibly small. In contrast with the curves for constant ionic strengths, the value of K_A' affects not only the pH value at which a given amount of acid is bound, but also the exact form of the relation between acid bound and pH. If K_A' is taken sufficiently small, the no-salt curve loses its characteristic steepness and becomes identical with the curves for constant ionic strength. Thus two additional means of estimating K_A' become available: (1) the difference in pH between the midpoint of the no-salt curve and any one curve at constant ionic strength; and (2), the extent to which the no-salt curves differ in slope from the curves at constant ionic strength. The value of K_A' selected for graphical representation in the no-added-salt curve of Fig. 6 (approximately 0.1) was chosen because it gives very nearly the proper separation from the other curves when the same value is substituted into the value of $\frac{K_A'}{a_{Cl}}$ attached to each of them.

The most exacting of the remaining tests which could be applied to the consequences developed from the postulates would be to attempt superposition of the several sets of data with the theoretical curves described by eq. 7 or 7'. These equations, however, were derived for the simplest case of monovalent acids; and wool, like other proteins, is highly polyvalent. This difference can have either of two results: (1) if all the dissociating groups have identical *intrinsic* dissociation constants and if they are far enough removed from one another in the molecule to exclude appreciable electrical interaction between them, the acid-combining curves, as Simms,[40] Weber,[51] von Muralt,[49] and others have shown, should be identical with those of a monobasic acid, and eq. 7 and 7' should be applicable. (2) If the groups are of unequal intrinsic strength, or if they are of equal intrinsic strength but are close enough to one another so that changes in distribution of electric charges, caused by partial dissociation, weaken the dissociating tendency of the remaining groups, the resulting acid-combination curve would be the sum of a number of smaller curves distributed along the pH axis. Conse-

quently it would be broader with respect to the pH axis than those predicted by the equations above.

In the direct comparison presented in Fig. 7, the estimated contribution of the imidazole groups (.03 millimole) has been subtracted from the acid-combination data in an effort to have them represent as nearly as possible only the dissociation of carboxyl groups.* As the figure makes clear, the corrected experimental curves, both in the presence and absence of salt, are broader than the theoretical ones, and the second of the two alternatives stated above must prevail.

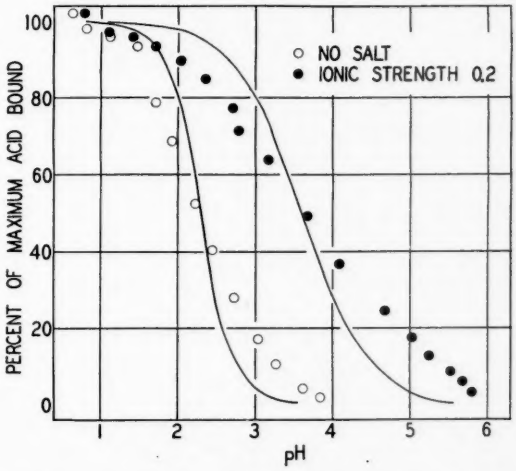

Fig. 7. The experimental data for acid combination as a function of pH compared with theoretical curves for a monoacid base (equations 7 and 7′). An estimated contribution from the histidine content of .03 millimole per gram has been subtracted from the experimental values, as described in the text.

The high degree of symmetry of the differences between the experimental and the theoretical curves suggests, however, that the experimental curve is not the sum of a small number of distinct groups of curves characterized by *widely different* dissociation constants, but is the result of a very regular kind of electrostatic interaction between ionic charges affecting the dissociation of groups which are all intrinsically similar. Earlier analyses of the acid-titration curves of other proteins [5, 8, 9, 10, 17] have been based on the opposite assumption of distinct groups characterized by widely different constants.

* The subtraction of a constant quantity is justified only at pH values more acid than those at which imidazole groups begin to give off hydrogen ions. In 0.2 *M* salt solutions, the correction should diminish appreciably at pH 5.4 and become zero at pH 6.4. Since the pH at which the correction should diminish in solutions low in salt or containing no salt cannot be estimated, recourse has been had to the subtraction of a quantity independent of pH. This results in varying degrees of over-correction at the low end of each set of data, but the effect is small.

The view suggested above is based on considerations similar to those which led Cannan to the same conclusion for the titration curve of egg albumin; it receives added support from the fact that the midpoint of the experimental curve (at high salt concentrations) occurs at a pH (4.0–4.1) which may be expected to characterize the dissociation of carboxyl groups in large peptides,[6] and by other considerations discussed below.

The regularity of the difference between the theoretical curve for a monovalent acid and the experimental curve is shown more clearly if the ordinates of all the curves, after subtraction of the estimated contribution of histidine, are changed from the acid bound to $\log \frac{A}{A_m - A}$ where A signifies the amount of acid bound at any pH and A_m is the maximum acid-binding capacity. The resulting graphs of the measurements at constant ionic strength, shown in Fig. 8, are close approximations to straight lines which are roughly parallel over a wide part of their total range. Deviations from this regularity appear only where the maximum and zero values are approached, but at both these extremes the quantity plotted is extremely sensitive to experimental error. In addition, the data may well deviate from this simple theoretical relation for acid combination as zero acid combination is approached, since the base combination function which begins to be of importance in this region has been left out of account. As a result of this additional factor, the curves must intersect at the base line within a narrow interval of pH, and cannot remain parallel.

The slope of the theoretical curve in Fig. 8 for constant ionic strength is — 1.0. The slopes of the lines through the experimental points for ionic strengths up to 0.2 are exactly — 0.50. Thus, a very simple relation exists between the experimental data and the theoretical curves which were derived on the assumption of a single dissociation constant for all the dissociating groups. The simplicity of this relation appears to support the view that the curve is the sum of a *continuous* series of curves for the individual dissociating groups, which differ in strength from one another by slight increments determined by some law of electrical interaction between their charges, rather than that the curve is the sum of a few groups of identical curves with widely different constants.

The slope of the theoretical curve for no added salt (eq. 7′) depends on the ratio of K_H' to K_A'. When $K_A' \gg K_H'$ (the more probable case with HCl) the slope approaches — 2. When K_A' is only ten times larger than K_H' the slope is still nearly — 2 for small amounts of acid bound but its absolute value becomes considerably smaller for larger amounts. However, the data obtained in the absence of salt, shown in Fig. 8, have a slope of very nearly — 1 when the amounts of acid bound are less than three-quarters of the maximum. For larger amounts bound, the slope approaches — 2. It is not surprising that the discrepancy between the simple theory and the measurements should be more serious and less regular in the absence of salt than at constant ionic strength, since the dependence of acid bound on hydrogen ion concentration in eq. 7′ or 7″ is essentially of higher degree than in eq. 7. The transition (involving a summation) from the simple equation for a monovalent acid to the proper polyvalent equation, is therefore more complicated.

The fact that over a great part of the pH range the slope obtained in the absence of salt is also just one-half of the value required by the equa-

tions has the fortuitous result that the experimental curve somewhat resembles the curve of the simple law of mass action for a monobasic acid." This approximate resemblance must be regarded as the resultant of the opposing effects of the steepening of the curve caused by simultaneous variation of hydrogen and chloride ions, and the broadening effect of electrostatic interaction between many identical dissociating groups.

The hypothesis that the departure of the individual experimental curves from the slopes predicted by eq. 7 and 7′ is caused solely by the high polyvalency of the wool protein, does not depend exclusively on the considerations just discussed. It is very strongly supported by the almost exact correspondence of the experimental curves for wool at high constant ionic strengths with the corresponding curves for egg albumin. When similarly plotted as $\log \frac{A}{A_m - A}$ against pH these data (at least for dilute salt solutions) also yield straight lines, with slopes which are also very nearly — 0.5. The same linear relationship between $\log \frac{A}{A_m - A}$ and pH has appeared in investigations of widely different dissolved substances which have in common only the properties of polybasicity and high-molecular weight. These substances include, among others, polyacrylic acid,[32] and certain nucleic acids.[23, 41] Kern has shown that, over a wide range of polymerization numbers, the slope of the linear relationship for polyacrylic acid is also almost exactly — 0.50.

2. *Alternative Analysis by the Donnan Equilibrium*

The difficulties inherent in application of the Donnan equations to the combination of wool fibres with acid have already been detailed. However, if a somewhat arbitrary selection of parameters is permitted, an alternative treatment for the restrictions on combination of acid due to the presence of two phases is possible, and a number of features of the present data can be described as direct consequences of the Donnan equations. In application of the Donnan equilibrium to fibres, a choice must be made between regarding the solid phase as a dispersed phase (in imbibed solvent), permeable to dissolved acid and salts, and the alternative view that it is a true solid phase in which the phenomena of acid combination take place in an external adsorption layer. The first of these models has been chosen as a basis for calculation, since the second offers no obvious basis for the assignment of any but arbitrary numerical parameters.

The result of this choice is given in Fig. 9, which shows calculated curves of acid combined by protein as $\log \frac{A}{A_m - A}$. In this calculation a single dissociation constant, 1×10^{-4}, and a protein concentration of 0.8 equivalent per liter have been used. The latter value bears a reasonable relation to the equivalent weight of wool, which is approximately 1250, and its moisture content at saturation of approximately 30% by weight. Although the relations of the curves calculated for no added salt and for different constant ionic strengths would be appreciably altered by the choice of other numerical values, their positions on the pH axis and the value of the maximum fix the relation of the dissociation constant to the equivalent concentration within fairly narrow limits. Activity coefficients have been neglected. The

ordinates of the curves represent only the acid reacting with the protein and do not include the acid which may be merely dissolved in the fibre phase. The latter should be practically negligible except in the immediate vicinity of the top of the curve.

It is immediately evident that the curves in Fig. 9 satisfy the requirements imposed by the data in three outstanding respects: (1) The curve for the case of no added salt is very similar to the experimental one; (2) the curves for constant ionic strengths are less steep than the curve for no salt, and their average slopes, although still too high, are nearer the experimental ones than the slopes given by eq. 7, which were twice as large as those required by the data; (3) when measured in the upper half of the figure, the dependence on ionic strength of the pH values at which a given amount of

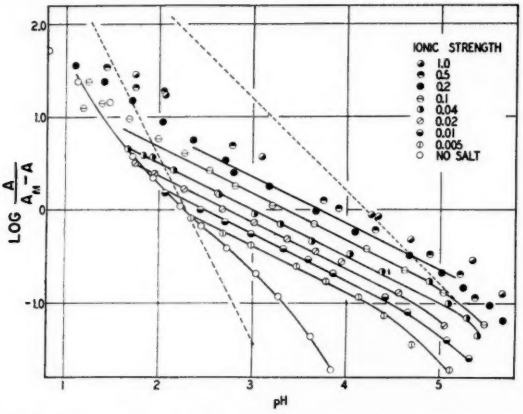

Fig. 8. The experimental data for acid combination as a function of pH and chloride concentration (corrected by subtraction of the estimated contribution of histidine) compared with the linear relations described by equations 7 and 7′. The straight lines through the experimental points over the range of approximately 5% to 90% of maximal combination were drawn with a slope of 0.5. The broken lines represent the theoretical equations for no-salt (7′) and for infinite salt (7) respectively.

acid is combined is approximately logarithmic when the ionic strengths are low; when the ionic strengths are high, the positions of the curves with respect to the pH axis approach a limit.

In another important respect, however, the curves of Fig. 9 are entirely different from those obtained by experiment or calculated from eq. 7 (shown in Fig. 8); the experimental curves are roughly parallel except at very high ionic strengths and as they approach closely to the base line. The curves of Fig. 9, on the contrary, converge continuously, and this convergence is inherent in any simple analysis by means of the Donnan equilibrium.

Another consideration must be taken into account, before accepting as significant the partial agreement of the Donnan equations with experiment. It has already been shown that there is a detailed agreement between the experimental data for wool and for dissolved egg albumin at moderate ionic

strengths. If significance were to be attached to the fact that the Donnan equations reduce the slope of the theoretical monobasic acid curve to a value considerably closer to its experimental value for wool, then it would seem necessary to conclude that the Donnan treatment must be applied also to egg albumin *in solution*. The further requirement that the application of the Donnan equations to the *dissolved molecules* must involve nearly identical numerical values for the parameters of the equations in the two physically quite distinct cases is even less acceptable.

The model which has been used as a basis for the application of the Donnan equations to the present experiments is intrinsically unreal. It is unlikely, for example, that all the water contained in the immersed fibres can be regarded as solvent water. Not only is it comparable in magnitude

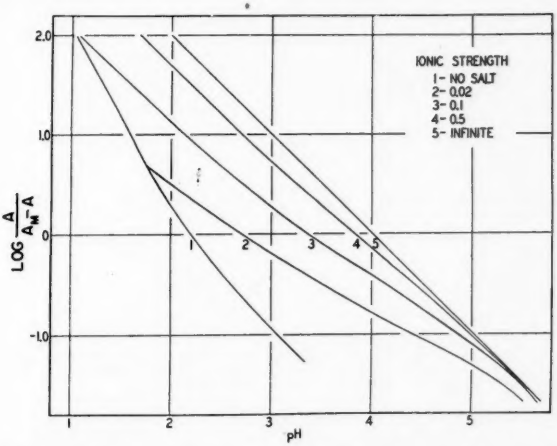

Fig. 9. The effect of different constant anion concentrations on the acid bound by a non-diffusible base as a function of pH. The parameters employed in the application of the Donnan equations are given in the text.

with the water of crystallization of proteins in general, but it corresponds closely with the hypothesis of definite and limited hydration of the polar groups or bonds of the wool molecule.* Such bound water can be regarded as a solvent medium only in a very restricted sense and it is hardly likely that acids or salts will distribute themselves between it and the external solvent medium in a simple one-to-one ratio. It has not proved possible to detect experimentally any combination with neutral salts when fibres containing half of the maximum amount of water which they can absorb are placed in 0.2 *M* KCl at pH 6.4. Thus, half or nearly half the maximum water content is not free to dissolve ionized acids or salts. This conclusion also results from a recent detailed study of moisture absorption of cotton fibres in this laboratory.[42]

* Unlike such cases as swollen gelatin to which the Donnan equations are more legitimately applied.

The principal distinction for practical purposes (such as the interpretation of acid dyeing) between the mechanism of acid combination proposed in this paper and the alternative treatment in terms of the Donnan equilibrium, lies in the expectation that the specific affinities $\left(\frac{1}{K_A'}\right)$ of different anions for wool may vary considerably. Conversely the experimental study of such a variation and its dependence on such variables as temperature and dielectric constant has considerable bearing on the views discussed here, and is at present in progress.

The authors are indebted to Charles H. Fugitt for many of the experimental measurements reported in this paper.

(Continued from Page 220)

Earl Constantine, president of the National Association of Hosiery Manufacturers, of the American Trade Association Executives, and a director of the Institute, was the principal speaker at Ohio State University's annual Institute for Trade Association Secretaries, March 18 and 19.

* * *

G. H. Conze, president, Susquehanna Silk Mills, has been re-elected president of the National Federation of Textiles, and M. K. Yorks, president, Bloomsburg (Pa.) Silk Mills, re-elected vice-president.

* * *

Alexis Sommaripa, manager, Fabric Development of the Rayon Division, E. I. du Pont de Nemours & Co., and Dorothy Nickerson, secretary, Inter-Society Color Council, were the speakers at the closing session of the Charlotte, N. C., meeting of Committee D–13, A. S. T. M., Mar. 14. Mr. Sommaripa spoke on "Quality Criteria for Spun Rayons," and Miss Nickerson on "The Standardization of Color Names."

* * *

Harold DeWitt Smith, treasurer of the A. M. Tenney Associates, Edward R. Schwarz, professor of textile engineering, Massachusetts Institute of Technology, and Alexis Sommaripa, manager, Fabric Development, Rayon Division, E. I. du Pont de Nemours & Co., are to present papers on synthetics at an afternoon session of the National Association of Wool Manufacturers, which is to celebrate its 75th anniversary at the Copley Plaza Hotel, Boston, April 4.

The Ideal Carpet Wool Tentatively Defined

A TENTATIVE GUIDE OF WOOL TYPE for carpet wools is one of the interesting results of a study of "Chinese Carpet Wools and Their Improvement," conducted at the Experiment Station, University of Wyoming, under the direction of Robert H. Burns, wool specialist, and reported under the above title by him, A. Johnston and W. C. Chen.

Chinese students studying at Wyoming had shown special interest in developing a program of wool improvement that would suit their environmental conditions, and it was decided that this could best be done by working in areas where management and feed conditions are unfavorable and by improving the native sheep by selection within their type. It was with this objective in view that the study was conducted. The resulting report is summarized by the authors as follows:

Summary

"Some of the different types of carpet wools are described as to their characteristics and origin.

"A series of samples were collected from carpet wool dealers and mills, and their opinions were obtained as to the relative value of the different samples as carpet wools.

"Seven samples of carpet wools and a sample of Romney wool were analyzed microscopically and macroscopically, for fibre type, fibre thickness, and fibre length.

"A tentative ideal type for carpet wools was set up for the use of wool producers in improving the type of wool produced by their native sheep by a process of selection within the type."

Ideal Carpet Wool Type

As a result of certain definite relationships that were found in this study the following tentative guide of wool type for carpet wools was set up:

"1. An ideal carpet wool should contain at least 15% by count or 35% by weight of heterotypical fibres. These fibres should have an average thickness of at least 12 ten-thousandths of an inch, and the fibre sizes should not vary more than 15%. The average length of these fibres should be at least 100 mm. for normal growth (12 months), and the variability of the fibre length should be less than 20%.

"2. An ideal carpet wool should contain not more than 2% by count or 4% by weight of kemp fibres. The dimensional characteristics of the kemp fibres are not so important. The important thing is to eliminate kemp from the fleece, and this can be done according to the experimental work carried out by Bryant * on Scotch Blackface sheep.

"3. An ideal carpet wool should contain not more than 85% by count or 65% by weight of true wool fibres. These fibres should have an average thickness of not to exceed 10 ten-thousandths of an inch, and their variation in fibre thickness should not exceed 25%. They should have an average length of at least 100 mm. for normal growth (12 months), and the variation in fibre length should not exceed 25%."

* Bryant, D. M., "A Note on the Inheritance of Kemp in Blackface Sheep." *J. T. I.*, Aug. 1933, P. T309–16.

Abstracts

Committee on Abstracts and Bibliography:
E. R. Schwarz, Chm., Dr. E. J. Saxl, C. H. Clark.

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Address, C. H. Clark, Sec., 65 Franklin St., Boston, Mass.

I. Fibres (Synthetic and Natural) and Fibre Analysis

Casein Fibre: Present Status of. E. O. Whittier and S. P. Gould. *Am. Dye. Rptr.*, Oct. 30, 1939, P. 641–2.

Paper presented at A. A. T. C. C. Annual Meeting, Boston, Sept. 16, 1939. (C)

Cellulose Fibres: Structure. H. Staudinger and F. Reinecke. *Kunstseide*, 1939, V. 21, P. 280–5; abs. in *J. T. I.*, Nov. 1939, P. A718.

The structure of cellulose is discussed and it is pointed out that the production of synthetic fibres, such as P. C. and Nylon fibres, confirms the view that the fibre properties of such natural cellulose materials as cotton, flax, etc., depend on the presence of long macro-molecules, not on biostructure. The degree of polymerization of the cellulose of natural fibres is about 3,000 while that of regenerated cellulose fibres is generally between 250 and 500. The strength of cellulose fibres increases with increasing degree of polymerization up to a degree of polymerization of about 800, further increases above this figure producing only slight increases. The viscosity of cellulose solutions increases almost proportionally with the degree of polymerization in the range 200 to 500 but at higher degrees of polymerization shows a much more rapid increase. Owing to the difficulty of spinning solutions of very high viscosity it has not been possible to produce rayons of degrees of polymerization of the same order as those of the natural cellulose fibres. Fibres of cellulose of a degree of polymerization of less than 200 are of little practical value. Tests on some nitro rayons of low strength showed

degrees of polymerization below 200. Nitrocelluloses of high degree of polymerization are readily obtainable but degradation always occurs in the denitration process. Cuprammonium rayon generally has a degree of polymerization of 500–550. The degree of polymerization of modern viscose rayon products is usually about 300, while certain special viscose staple fibre products have degrees of polymerization of the order of 500. Tables are given showing the degrees of polymerization, strengths, etc., of various regenerated cellulose rayon and other fibres. (C)

CELLULOSE XANTHATE: REACTIONS OF—AND THEIR TECHNOLOGICAL IMPORTANCE. Stefan Poznanski. *Rayon Textile Mo.*, 1939, July, P. 57–9; Aug., P. 47–9; Sept., P. 70–2.

Results of a research designed to explain the mechanism of action of the spinning bath on viscose. (C)

COTTON STAPLING: MODERN. Part I. Anon. *Saco-Lowell Bulletin*, Oct. 1939, P. 19–26.

In this article is discussed some of the limitations of hand stapling, and a laboratory method for fibre length analysis which has been found to be quite rapid, accurate, and practical for modern cotton mill usage is described. (C)

COTTONS OF EGYPT. H. A. Hancock. *J. T. I.*, Oct. 1939, P. P412–28.

Recent trends in the Egyptian crop with regard to staple length, yield, grade, and uniformity of staple, are indicated and discussed. Staple characters, quantities of cotton available, yarn strength and counts spinnable are tabulated for the several varieties and grades, and discussed from the spinner's point of view. (C)

DEGREASING OF CRUDE WOOL: CAUSES OF THE DAMAGING EFFECT OF FAT SOLVENTS IN THE—BY BENZINE AND TRICHLORETHYLENE. Eduard Langer. *Spinner u. Weber*, 1939, No. 21, P. 35–6; abs. in *C. A.*, 1939, V. 33, Col. 9654.

In degreasing, the solvent should not be longer than 20–30 min. in contact with the wool at 45°. Wool should never be degreased completely; three baths should be used with 40, 20 and 10% fat content so that the wool retains 0.5–0.8% fat; no steam should be employed for the removal of the solvent or for drying; the temp. of the moist air should not exceed 45°. Org. solvents give the product a better appearance than does an aq. wash, make it possible to recover the wool fat and wool sweat and render it unnecessary to use soaps, soda, etc. Wool fat and wool solvent can be recovered completely by extn. (C)

ELECTRICAL PROPERTIES OF STAPLE FIBRES. Fritz Weidmann. *Kunststoffe*, 1939, V. 29, P. 133–6; abs. in *C. A.*, 1939, V. 33, Col. 9652.

Graphs show that the elec. resistance of rayon fibres (viscose, cuprammonium and acetate) decreases with decreasing relative humidity and with rising temp. Dyeing increases elec. resistance somewhat. Owing to its lower moisture content at any particular relative humidity, acetate rayon has a considerably greater elec. resistance than the other two types of rayon tested. (C)

FIBRE CONTENT OF VARIOUS PLANTS. G. Bredemann. *Faserforschung*, 1939, V. 14, P. 105–12; abs. in *C. A.*, 1939, V. 33, Col. 8999.

Tables are given showing the results of studies on some 90 different plants. (C)

FIBRES: PROPERTIES OF. C. L. Wall. *Text. Mfr.*, Nov. 1939, P. 496–8, 500.

The strength, extensibility and other properties of fibres are considered by the author on the basis of the atomic structure of the fibres. (C)

JUTE: SCIENCE OF. S. G. Barker. *J. T. I.*, Sept. 1939, P. P273–304.

A very complete and accurate outline discussion of existing and needed scientific knowledge of the chemical and physical properties of jute. (C)

JUTE FIBRES: OBSERVATIONS ON SWELLING OF. W. G. Macmillan. *J. T. I.*, Sept. 1939, P. P305–10.

The methods of determining swelling are described, and it is noted that "results seem to indicate that swelling diminishes with increase of diameter —at first very rapidly, and then more slowly, and may eventually reach a point at which a theoretical diameter of no swelling is obtained." (C)

II. YARNS AND FABRICS

LINEN WEAVING PROBLEMS: RESEARCH OF. H. Boffey. *Text. Mfr.*, Aug. 1939, P. 346.

A broad survey of linen weaving problems and the relationship of research to them. (C)

MERCERIZED COTTON: MOISTURE RELATIONS. F. I. Bogoiavlenski. *Utschen. Zap. Univ. Kazan*, 1938, V. 97, P. 83–93 (through *Brit. C. A.*, 1938, V. AI, P. 511); abs. in *J. T. I.*, May 1939, P. A338.

The hygroscopicity of mercerized cotton rises to a maximum when the mercerizing alkali is 4*N* caustic soda or 6*N* caustic potash. The maximum is 1.6 to 1.7 times that for raw cotton. Hysteresis is also greatest at these concentrations. (C)

NATURAL FELTS: MANUFACTURE OF. J. Colin Schofield. *Wool Rec. & Text. Wld.*, June 15, 1939, P. 1323–9.

After describing the processing of natural felts, the author expresses the opinion that "Experimentation on the felting process as exhibited in the making of natural felts is a novel development and is bound to yield results of great technical importance as this scientific and theoretical side is revealed." (C)

OPEN-WIDTH WASHING OF FABRICS: NEW METHOD OF. Spooner Dryer and Engineering Co., Ltd. *Text. Mfr.*, Sept. 1939, P. 400–401.

Water is forced through nozzle slits against both sides of the cloth in a new type of soaping or washing-off machine. (C)

POLISHING AND GLAZING OF YARNS AND TWINES. W. I. Finnetney. *Cotton*, Aug. 1939, P. 61–2, 66. (C)

PROCESSING OF RAYON STAPLE FIBRE (IN BRIEF AND CONDENSED STATEMENTS). Heinz Speier. *Rayon Text. Mo.*, 1939, May, P. 56–7; June, P. 61–2, 64; July, P. 67–8; Aug., P. 59–60. (C)

QUALITY PRODUCTION CONTROL IN THE MILL. W. L. Bentley. *Rayon Text. Mo.*, May 1939, P. 45–6; June, P. 71; July, P. 61–2; Sept., P. 78–9; Nov., P. 64–5.

A compendium of essential facts relative to this important subject. The author states that the object of quality production control is to protect the mill against claims and returns, and discusses the subject with particular reference to rayon greige goods. (C)

RAYON CRÊPE RESEARCH. VII. EFFECTS OF SOME VARIATIONS IN DYEING AND FINISHING UPON THE PEBBLE OF RAYON CRÊPE FABRICS. *Am. Dye. Rptr.*, May 29, 1939, P. 289–92.

This is Part VII of the Rayon Crêpe Research which is conducted jointly by the Throwsters Research Institute, Inc., and the A. A. T. C. C. (C)

RAYON FILAMENTS: MECHANICAL PROPERTIES. Y. Konisi. *J. Soc. Chem. Ind. Japan*, 1938, V. 41, P. 438–41B; abs. in *J. T. I.*, May 1939, P. A338.

The following characteristics of rayon filaments are mathematically discussed—(1) the apparent modulus of elasticity and apparent tensile strength in the wet and dry states; (2) the relationship between the apparent mechanical properties and the surface tension of the impregnating liquid; and (3) the tensile strength correction factors for various atmospheric humidities, and the micellar orientation in rayons. (C)

RAYON WARP SIZING MACHINE. G. Rammer. *Leipz. Monats. Text. Ind.*, 1939, V. 54, *Fachheft* I, P. 23–6; abs. in *J. T. I.*, May 1939, P. A313.

The disadvantages of hank sizing processes and of the use of warp sizing machines with drying cylinders for rayon are pointed out and an account is given of a warp sizing machine in which the drying is effected by means of hot air. (C)

RAYON WARP SLASHING: CONTINUOUS FILAMENT. W. L. Bentley. *Text. Age*, Dec. 1939, P. 42–7.

The author indicates the size concentrations for the different deniers and cloth constructions of both viscose and acetate rayons, and presents his opinions as to sizing materials and their properties. (C)

RAYON VS. WOOL. "Borderer." *Silk J. & Rayon Wld.*, 1939, Mar., P. 19, 23; May, P. 27–8.

Can wool ever be replaced by a rayon substitute? The answer depends on that to another question: Why does wool felt? and this article reviews the facts and makes the answer possible. (C)

RAYON: REDUCING WEAVING DIFFICULTIES; CAUSES OF FILAMENT BREAKAGES. Denier. *Silk J. & Rayon Wld.*, May 1939, P. 14–5.

The author points out that the majority of filament breakages are, directly or indirectly, due to the reed, and discusses the most suitable types of reeds to use and the factors affecting them. (C)

ROT PROOFING OF JUTE. H. A. Elkin and W. A. S. White. *Text. Mfr.*, Sept. 1939, P. 394; *J. T. I.*, Sept. 1939, P. 340–6.

The rot-proofing of jute is a problem to which scientific investigators gave very little attention until comparatively recently. This was probably due to economic factors. (C)

RUNNING CUT STAPLE RAYON FIBRE: PRACTICAL METHODS OF. I. DESCRIPTION OF THE FIBRES. *Cotton*, 1939, Aug., P. 63–6; Sept., P. 52–5; Nov., P. 54–5, 57.

A series of articles on the manufacture of yarns and fabrics from cut staple rayon. The first article points out the general properties of the synthetic fibres; later articles take up actual manufacturing problems. (C)

SHRINKAGE: INCIDENCE OF—IN WEARING APPAREL FABRICS. Anne B. Searle with Pauline Beery Mack. *Am. Dye. Rptr.*, Aug. 7, 1939, P. 405–9, 439. (C)

WARP TENSION: INFLUENCE OF VARYING—ON SOME PHYSICAL PROPERTIES OF PLAIN COTTON CLOTH. W. E. Morton and R. Williamson. *J. T. I.*, Oct. 1939, P. T137–56.

The contents of the paper are summarized as follows: (1) The influence of varying tension has been examined for a series of plain square cloths woven from two-fold yarns in a 56 reed and having cover factors ranging from 13.2 x 13.2 to 16.2 x 16.2 nominal. (2) The changes in the thread spacing as the fabric moves from the fell to the cloth roller have been noted, and the forces operating during this period are discussed. (3) Varying the warp tension was found to give rise only to relatively small changes in weft crimp, but for cover factors 14 x 14 and over the effect on warp crimp was considerable. (4) With cover factor 13.2 x 13.2 the cloth was predominantly weft crimped; with cover factor 16.2 x 16.2 it was predominantly warp crimped; but between these the cloth could be either one or the other depending on the warp tension. The range of fabrics woven thus straddled the critical and very important condition in which the whole character of the cloth may be altered simply by varying the warp tension. (5) Arising from the differences in balance of crimp, considerable differences were noted in the breaking extension, breaking load, and bursting strength of those fabrics having cover factors over 14 x 14, and it is concluded that in weaving densely set fabrics careful attention must be paid to warp tension if uniform cloth is to be produced. (C)

III. CHEMICAL AND OTHER PROCESSING (NOT OTHERWISE CLASSIFIED)

CELLULOSE ACETATE RAYON DYES: APPLICATION. E. Hermann. *Monatsh. Seide u. Kunstseide*, 1939, V. 44, P. 234–6; abs. in *J. T. I.*, Sept. 1939, P. A577. (C)

CELLULOSE: CHEMICAL MODIFICATION OF—WITH SOME OBSERVATIONS ON THE MORE RECENT DEVELOPMENTS IN TEXTILE FINISHING PROCESSES. J. Craik and W. R. Davis. *J. Soc. Dyers Col.*, Dec. 1939, P. 597–606.

The paper deals mainly with the general trend in the development of cellulose derivatives, and some of the newer finishing processes, but it also gives an outline of the older and better known products. (C)

CELLULOSE: REDUCING ACTION IN ALKALINE PRINTING MEDIA. *Ciba Review*, 1939, No. 22, P. 791–2; abs. in *J. T. I.*, Sept. 1939, P. A579.

Attention is directed to the possibility that cellulose itself may act as a reducing agent in alkaline printing media. Thus, Cibanone Blue is completely fixed on cotton if printed with caustic soda (106° Tw.) alone and steamed. Discharge salt W. is effective in reducing some indigoid and anthraquinone dyes even without sulphoxylates, if the mixture is made alkaline with Na or K hydroxide or carbonate. (C)

CHEMICAL DEVELOPMENTS IN THE TEXTILE INDUSTRY: IMPORTANT. E. W. K. Schwarz. *Am. Dye. Rptr.*, Jan. 8, 1940, P. 6–8, 19–21.

A comprehensive review of recent developments presented at December meeting, A. A. T. T. (C)

CHEMISTRY OF SILK AND SILK PROCESSING: RECENT DEVELOPMENTS IN. Walter M. Scott. *Am. Dye. Rptr.*, Sept. 4, 1939, P. 501–2, 546–50.

This article is the sixth in a series of reviews which have appeared in this journal under the same title. These reviews summarize the progress which has been made in the fundamental chemistry of the silk fibre and in the chemical processes which play a part in the transformation of the raw silk into the finished product. The present review brings the story up to September 1939. (C)

DYEING OF ACETATE RAYON AND OF ACETATE RAYON MIXED FABRICS. Werner Steger. *Klepzig's Textil-Z.*, 1939, V. 42, P. 371–5, 382–3; abs. in *C. A.*, 1939, V. 33, Col. 3161, 8998.

A detailed description of the sensitivity of the fibres toward the temp. of the washing bath, of dyeing with celliton dyes and of the dyeing of mixed fabrics. Many dyes are listed which are suitable for dyeing acetate rayon, silk, semi-wool, etc., and various recipes and suggestions are given. (C)

DYEING APPARATUS WITH CIRCULATING DYE BATH FOR PIECE GOODS. Woldemar-Fehrmann. *Mell. Textilber.* (German edition), 1939, V. 20, P. 218.

The completely closed app. consists of three cylindrical vessels, and accessory equipment. Compressed air is used to force the dye bath through the goods, a special device ensuring even distribution. This app. is especially useful for dyeing or treating rayon, staple rayon or other textiles showing similar swelling tendency. (C)

DYED STAPLE FIBRES: CAUSES AND PREVENTION OF STRIPINESS. (1) A. Schejnoha. (2) H. Brandenburger. *Zellwolle*, 1939, V. 5, P. 156–9; abs. in *J. T. I.*, Sept. 1939, P. A578.

(1) It is pointed out that stripe effects in piece-dyed staple fibre fabrics may have their origin in processes prior to dyeing. Various common causes such as the mixing of different lots of staple fibre, and faults in the preliminary and weaving processes arising from unsatisfactory work on the part of the weaver and from defective mechanisms and incorrect settings are discussed. (2) The importance of efficient desizing is pointed out and methods of detecting traces of size are outlined. Precautions to be taken

in desizing, washing, bleaching, mercerizing and dyeing processes in order to avoid uneven dyeing are described and the selection of dyes and dyeing apparatus is discussed. (C)

DYEING OF WOOL BY THE ADSORPTION METHOD. S. S. Rakhlina. *Shersty-anoe Delo*, 1937, V. 16, No. 1, P. 30–47 (through *C. A.*, 1939, V. 33, Col. 4789); abs. in *J. T. I.*, Sept. 1939, P. A578.

Insoluble alizarin dyes, such as Alizarin Yellow, Alizarin Red, Alizarin Orange and Amino-alizarin are strongly adsorbed by wool fibres from their aqueous suspensions. Adsorption is rapid from neutral and acid media, especially so from the latter. The adsorption process of wool dyeing proceeds in two phases, the labile and the stable. Treatment of the moist wool with the aqueous suspensions of the dye in the cold (up to 22°) for 10 min. is sufficient for labile dyeing. Stabilization is attained in the second phase by treatment in the vat with an acidified solution of sodium or potassium chromate (up to 1%) for 15 min. Adsorption of the dye (labile phase) can be rendered slower by reducing the temperature and the acidity. The addition of saponin or gelatin reduces the velocity of adsorption of the dye on the wool fibres but improves the fastness to rubbing. The bath must be acidified with organic acids (formic, acetic). With the exception of Alizarin Yellow, the use of sulphuric acid results in uneven dyeing. Of the insoluble alizarin dyes investigated, good fast colors were obtained with Alizarin Yellow, Alizarin Red No. 1 and Alizarin Bordeaux. Alizarin Orange was not fast to light and Amino-alizarin was not fast to rubbing. (C)

DYEING OF STAPLE AND SPUN VISCOSE RAYON. Charles B. Ordway. *Am. Dye. Rptr.*, Oct. 16, 1939, P. 613–5.

A discussion of dyeing methods used in the past on cotton and how they have been applied on staple and spun viscose rayons. The physical and dyeing properties encountered in the processing of staple and spun viscose rayons. (C)

DYESTUFFS: WHAT—SHALL I USE? W. E. Batson. *Text. Recorder*, 1939, June 6, P. 43, 45; July 6, P. 40.

The author discusses the merits and demerits of the various types of dyestuffs in their application to silk. (C)

ELECTROLYTIC DISSOCIATION: THEORY OF. C. G. Hampson. *Dyer*, 1939, V. 82, P. 103–5, 141–2, 140; abs. in *C. A.*, 1939, V. 33, Col. 9652.

The significance of pH in textile-plant operations is considered. (C)

EMULSIFICATION OF (JUTE) BATCHING OILS. Alexander King. *J. T. I.*, Sept. 1939, P. P379–86. (C)

FABRIC TREATMENT: EFFECT OF ALMOST FREE ALKALI IN. C. Bergell. *Seifens.-Ztg.*, 1939, V. 66, P. 425 (through *Brit. Chem. Abs. B.*, 1939, V. 58, P. 932); abs. in *J. T. I.*, Nov. 1939, P. A724.

It is found that part (approximately two-thirds) of the alkali in metasilicate solutions behaves as "free alkali" as regards damage to textile fabrics, *e.g.*, 0.25*N*-metasilicate caused rather more weakening of threads

containing wool than did 0.125*N*-caustic soda under the same conditions (1 hr. washing at 50° C.). (C)

IMPREGNATION OF STAPLE RAYON AND RAYON. Karl Mickseh. *Zellwolle u. Deut. Kunstseiden-Ztg.*, 1939, V. 5, P. 118–20, 162–4; abs. in *C. A.*, 1939, V. 33, Col. 9655.

Suggestions and various recipes are given for water- and flame-proofing impregnations. (C)

JUTE: DYEING OF. D. Carter. *J. T. I.*, Sept. 1939, P. P328–39. (C)

LIGHT: EFFECT OF—ON ERYTHROSIN AND BROMO ACID (TETRABROMOFLUORESCEIN). O. L. Evenson. *J. Assoc. Official Agr. Chem.*, 1939, V. 22, P. 773–7; abs. in *C. A.*, 1940, V. 34, Col. 267.

Aq. solns. of erythrosin fade rapidly when exposed to direct sunlight, while the fading in 47.5% alc. is much slower. I appears to be liberated from the erythrosin mol. and Br from bromo acid by the action of light. Certain other dyes, in the presence of erythrosin, are destroyed, as a result of the action of light on the erythrosin present. (C)

LINEN PIECE GOODS: PROCESSING (DYEING) OF—IN THE U. S. O. W. Clark. *Am. Dye. Rptr.*, Dec. 11, 1939, P. 709–14, 727–9. (C)

METALLIZED ACID AZO DYES. M. L. Crossley. *Am. Dye. Rptr.*, Sept. 4, 1939, P. 487–8, 492.

Discusses the scientific and technical problems involved in the development of this type of dyes. (C)

MICROSCOPIC OBSERVATIONS ON WOOL DYEING. H. E. Millson, G. L. Royer and M. E. Wissemann. *Am. Dye. Rptr.*, Oct. 30, 1939, P. 632–8.

Presentation of this paper at the Boston meeting of A. A. T. C. C. Sept. 16 was illustrated with about 60 colored slides taken by the Kodachrome process. In this publication a few of these are reproduced in black and white to help with the explanation of the phenomena discussed. (C)

PERMANENT SOFTENING AGENTS (WITH SPECIAL REFERENCE TO CATIONIC SOFTENERS AND FINISHES). H. H. Mosher. *Am. Dye. Rptr.*, Sept. 4, 1939, P. 484–6. (C)

PEROXIDE BLEACHING. H. G. Smolens. *Am. Dye. Rptr.*, Sept. 4, 1939, P. 495–6, 498.

Relates mainly to peroxide bleaching of cotton materials. (C)

IV. RESEARCH METHODS AND APPARATUS

COLORS: METHOD OF DESIGNATING. Dean B. Judd and Kenneth L. Kelly. *N. B. S. J. Rsch.*, Sept. 1939, P. 355–85, RP1239.

A method of designating the colors of powdered drugs and chemicals and crude whole drugs has been described; this method has, furthermore, been devised with the thought of its applicability to colors of opaque, nonmetallic surfaces generally. Suggestions for its extension to the color

designations of transparent and translucent media have also been given. This method is dedicated to everyone who has found it difficult to make his color descriptions intelligible, in the hope that it will eventually be elaborated into a successful system of color designation for the general use of science, art, and industry. (C)

COTTON, STAPLE FIBRE, LANITAL AND WOOL YARNS: THERMAL CONDUCTIVITY. *Boll. Assoc. Ital. Chim. Tessile Color.*, 1939, V. 15, P. 81–6; abs. in *J. T. I.*, Nov. 1939, P. A720.

The thermal insulating power of various yarns has been compared by wrapping them round a copper cylinder containing warm water and observing the rate at which the temperature falls. If the value for the conductivity of wool is taken as 100, the other values are Lanital 111, Cisalfa 165, staple fibre (Superlena) 198 and cotton 235. (C)

COTTON YARNS: STRENGTH. J. Wiernsberger. *L'Ind. Text.*, 1939, V. 56, P. 164–5, 270–1; abs. in *J. T. I.*, Nov. 1939, P. A720.

An equation is deduced for the maximum theoretical strength of a cotton yarn and it is pointed out that actual mean strengths of cotton yarns made from Sakel, American and Indian cottons should reach 0.85, 0.6 and 0.5, resp., of the theoretical values under specified conditions of twist, etc. The ratio of minimum to mean strength, and the regularity of strength expressed by the ratio of sub-mean to mean strength are discussed and data are given for various types of yarns. (C)

DARK LIGHT. Francois Dervaux. *Teintex*, 1939, V. 4, P. 456–60; abs. in *C. A.*, 1939, V. 33, Col. 9002.

Analytically, dark light (invisible radiations) can be used for the detection of various fibres because they fluoresce differently; lanital and wool give a blush white, Cisalfa a brown, Fibramine a violet-brown, viscose appears dull and lusterless, cotton gives a violet-white, silk a bluish white more intense than wool, raw silk a yellow because of the grit, immunized wool a white, celanese a violet, Rhodiacéta an orange-yellow, copper silk a pale yellow and mercerized cotton a light brown; several others are also included. Another means of identification consists of first dyeing the fibres with a mixt. of Bright Green, Methylene Yellow N and (for animal fibres) Sulfoflavine FF and Acid Rhodamine NB and then comparing the colors of the dyed fibres in ordinary light and dark light. For example, Rhodiacéta gives a light green in ordinary light and a sky blue-gray in dark light. Other fibre examples are given. The fluorescence of oils, gum spots, papers and dyes is also discussed. (C)

ELECTRICAL AND GRAVIMETRIC MOISTURE CONTROL METHODS: COMPARISON. P. Lippke. *Kunstseide*, 1939, V. 21, P. 316–20; abs. in *J. T. I.*, Nov. 1939, P. A719.

The results of moisture content determinations in a staple fibre factory by an electrical measuring system through which the whole output of the drying plant passes and by gravimetric tests on 200 g. samples are compared. Considerable discrepancies are observed. Gravimetric tests with samples of different sizes showed variations in moisture content with size of sample, the results obtained with large samples (1,000 g.) generally agree-

ing well with those obtained by the electrical method. When it is desired to standardize or calibrate electrical devices by means of gravimetric tests, samples must be taken at intervals of 2 or 3 minutes, immediately before or after the measuring point; each time a small flake of 10 or 15 g. is extracted by hand until a sample of 1,000 or 1,500 g. is built up. In order to avoid loss or taking up of moisture, the samples must be tightly pressed against one another and immediately placed on the grate or in conditioning compartments. The determination of the moisture content should follow as soon as possible after the taking of the sample. The drying process must be so conducted that fresh air, kept at a temperature of 110° C. will be discharged, by means of a blower, against the whole mass of the staple fibre. (C)

EXPERIMENTAL SLASHER. Walter T. Schreiber and Omar C. Moore. *Text. Wld.*, July 1939, P. 62.

Developed at Alabama Polytechnic Institute for testing size formulas and sizing conditions; is stated to be economical and reliable in results. (C)

FAT RESIDUES IN THE TEXTILE FIBRE: DETERMINATION OF. W. Schulze. *Spinner u. Weber*, 1939, V. 57, No. 13, P. 52–3; abs. in *C. A.*, 1939, V. 33, Col. 8999.

The origin of fat residues in fibres is discussed and simple methods are given for extn. and detn. of the fat. (C)

V. PURE SCIENCE, ECONOMICS AND MISC.

COLOR FILM IN PHOTOMICROGRAPHY. K. John. *Phot. Korr.*, March 1939, V. 75, P. 38–41; abs. in *Eastman Kodak Abs. Bull.*, August 1939, P. 423.

The author lists various purposes for which a convenient and accurate color method is desirable, and gives the results of a series of investigations with Agfacolor film as the material; the latter as follows: (1) General definition is good for low-power, less satisfactory for medium-power, and rather poor for high-power photomicrography. (2) Differentation of fine color shades depends on the colors concerned, but is not as satisfactory as would be desired. (3) In general, the accuracy of color reproduction is not high, although this varies with the hue being reproduced. (S)

COTTON BALES: UPTAKE OF MOISTURE. P. S. H. Henry. *Proc. Roy. Soc.*, 1939, V. A171, P. 215–41; abs. in *J. T. I.*, Aug. 1939, P. A540.

Equations are derived for diffusion in absorbing media, in connection with the uptake of moisture by cotton bales. The problem comprises the diffusion of one substance through another in the pores of a solid body, which may absorb and immobilize some of the diffusing substance, with evolution of heat, which diffuses through the medium and affects the extent to which the solid can absorb the diffusing substance. There are thus two diffusion processes symmetrically coupled by the mutual interaction of the diffusants. The general solution of the problem is shown to be a linear combination of solutions to the ordinary diffusion equation with the same boundary and initial conditions but different diffusion constants. A new solution of the ordinary equation for diffusion into a rectangular paral-

lelepiped is given and also a table of data for diffusion into a plane sheet from which values for a parallelepiped can be deduced. (C)

CYSTINE CONTENT OF DEAMINIZED PROTEINS. W. C. Hess and M. X. Sullivan. *J. Biol. Chem.*, 1939, V. 128, P. 93–99; abs. in *J. T. I.*, Aug. 1939, P. A558.

The cystine content of deaminized proteins (casein, lactalbumin and wool) as determined by the Sullivan method is markedly lower than that of the corresponding untreated proteins. The other methods except that of Folin and Marenzi which gave very high values for the deaminized proteins indicated that the cystine content of the deaminized proteins was much the same as that of the untreated proteins. Evidence is given that by the action of nitrous acid on proteins the cystine value by the Sullivan method is lowered, because the amino group of the combined cystine is altered. (C)

DRYING: USE FOR—OF NEAR INFRA-RED RADIATION. L. S. Ickis and H. Haynes. *Gen. Elec. Rev.*, 1939, V. 42, P. 145–9.

A 250-watt drying lamp has been designed to supply the energy which is most effective for vaporizing the common solvents and washes used in lacquers. Reflecting equipment and ventilation are described and applications in drying tunnels for automobile bodies, lacquers, quick-drying enamels and baking enamels of the glycerol-phthalate type are dealt with. (C)

ELECTRIC AIR-PURIFYING AND FIBRE-RECOVERING APPARATUS. O. T. Koritnig. *Monatsch. Seide u. Kunstseide*, 1939, V. 44, P. 50–2; abs. in *J. T. I.*, May 1939, P. A344.

In the electric method for the purification of air or gases the air is caused to flow through a dust chamber between one or more charged electrodes and one or more earthed tubes or plates. Dust and other impurities in the air collect on the plates or tubes. Practical arrangements, power requirements, and the advantages of this method are briefly discussed. The method may be applied to the recovery of waste fibre in the air of spinning mills. (C)

FIBRE STRUCTURE X-RAY DIAGRAM: CALCULATION. C. Matano. *Pro. Phys. Math. Soc. Japan*, 1939, V. 21, P. 14–20 (through *Sci. Abs.*, 1939, V. 42A, P. 335); abs. in *J. T. I.*, Aug. 1939, P. A557.

The intensity distribution of Debye rings due to general fibre structure is calculated by using the conception of reflection of X-rays by the crystallographic plane and of diffraction by the zone in each crystallite as a unidirectional grating when the beam of X-rays is projected obliquely to the fibre axis. Calculated and experimental values for simple ring fibre structures are compared. (C)

JUTE: MINIMUM MOISTURE REGAIN FOR THE DEVELOPMENT OF MICRO-ORGANISMS ON. L. D. Galloway. *J. T. I.*, Aug. 1939, P. T127–30.

The experiments described indicate that the safety limit of moisture regain is approximately 17%, corresponding to an equilibrium with a surrounding atmosphere of *circa* 80% relative humidity. In order to attain a consistent measure of moisture content the regain of oil of jute was calculated on the dry weight of the fibre present less oil. The jute used was ordinary white jute and the fabric tested was 40″ 10 oz. hessian. (C)